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THE UNIVERSITY OF ALBERTA

THERMOLYSIS OF
4-METHYLENE-1-PYRAZOLINES

BY

© LOUIS M.H.C. SCHRIJVER

A THESIS
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

THERMOLYSIS OF 4-METHYLENE-1-PYRAZOLINES

submitted by LOUIS M.H.C. SCHRIJVER in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

The isomeric pyrazolines, 3-methyl-4-methylene-1-pyrazoline (I) and 4-ethylidene-1-pyrazoline (II), have been synthesized and characterized. The thermolysis of I at 175° gave 79.58% of 2-methylmethylenecyclopropane (III) and 20.42% of ethylidenecyclopropane (IV). Thermolysis of II at 175° gave III and IV in yields of 89.65% and 10.35%. The data have been corrected for the interconversion of III and IV under the thermolysis conditions. From the product ratios it is demonstrated that the mechanism does not involve solely a planar, nor an orthogonal trimethylenemethane intermediate. It appears that there is no single mechanism in the product formation from 4-methylene-1-pyrazolines.

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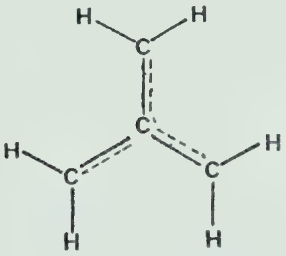
HISTORICAL

(A) Trimethylenemethane

Trimethylenemethane (TMM) has proved to be of considerable theoretical, synthetic (1), and mechanistic interest.

Early HMO calculations (2a,b) showed TMM to be a diradical in the triplet state with a large delocalization energy and very reactive termini.

However, recent MINDO/2 calculations of Dewar and Wasson (3) have shown that both triplet and singlet states are possible for TMM.



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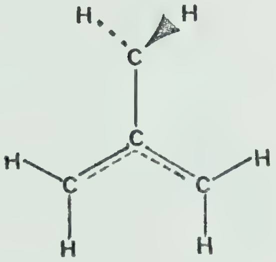

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MINDO/2 calculations of ΔH_f° were carried out on a closed shell singlet structure S_o, triplet (T_1), and open shell singlet (S_1), which has two unpaired electrons of opposite spin, for different angles (Θ) of twist of one terminal out of coplanarity with the others. (Θ = 0° for **1**, Θ = 90° for **2**). The results are shown in Figure 1.

The diagram shows that triplet TMM is the most stable structure and that the planar geometry is most fav-

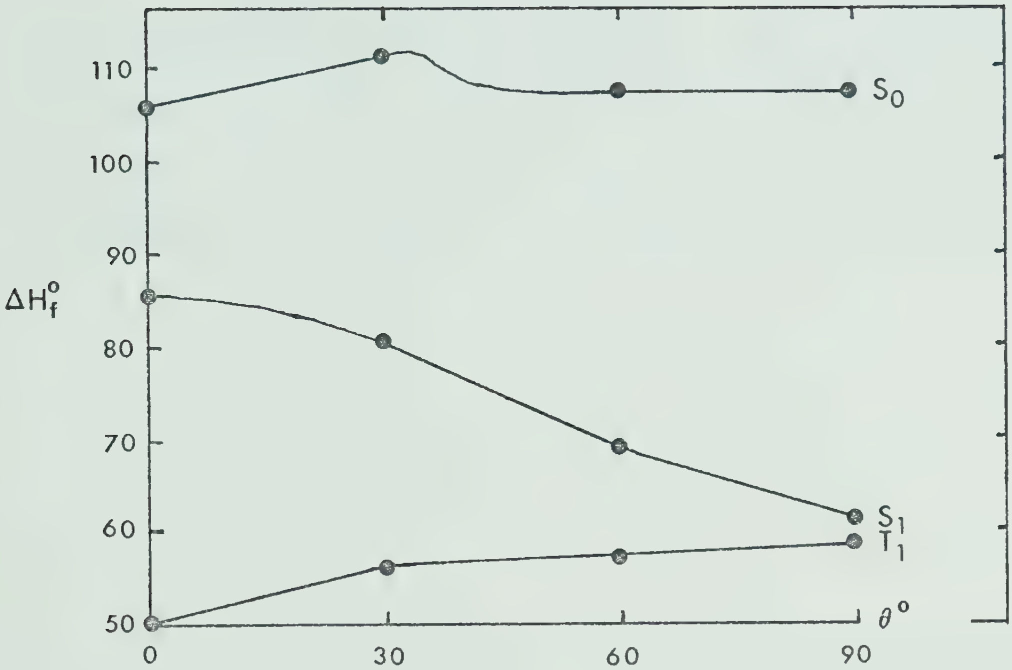
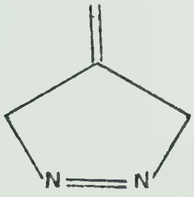


Figure 1. Dependence of Heat of Formation on Twist Angle (Dewar, 3).

ourable. In the perpendicular form, however, S_1 is not much less stable, although the planar form is clearly unfavourable. The authors conclude, that a process which leads to the singlet electronic configuration will produce an open shell ground state singlet of the orthogonal form **2**.

These results have been confirmed by experiment. In a recent esr study by Dowd (4) the TMM diradical signal was detected when 4-methylene-1-pyrazoline (**3**) was photolyzed at -185° (4b). A much stronger and cleaner signal was obtained by photolysis of 3-methylenecyclobutanone (**4**) (4c,d).



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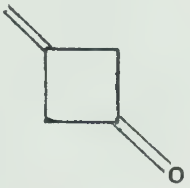

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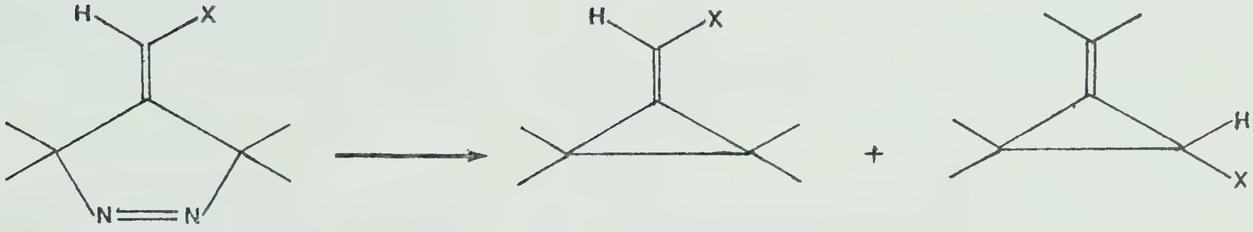
In the pyrolysis of 4-methylene-1-pyrazoline (**3**) Crawford and Cameron (5) concluded that TMM was formed on the basis of the equivalence of termini from deuterium labelling experiments.

The results of Dowd and Crawford have also been accounted for by the theoretical calculations of Borden (6), who also concluded that singlet TMM will likely ring close much faster than perform intersystem crossing to triplet TMM.

Doerr and Skell (7) found a high yield of 1.4-dimethylenecyclohexane and isobutene in the gas phase reaction of 2-iodomethyl-3-iodopropene. This could be readily explained

by assuming a triplet TMM intermediate, which dimerizes to give 1,4-dimethylenecyclohexane and also abstracts hydrogen to give isobutene. A singlet intermediate should mainly yield methylenecyclopropane through ring closure of which very little was found in Skell's work.

The photolysis of some 4-alkylidene-1-pyrazolines (5a,b) was investigated by Andrews and Day (8).



5a X = Cl
5b X = OOCEt

6

7

Their results are given in Table I.

In the photosensitized photolysis triplet TMM is formed, and gives product distributions close to the statistical ratio of 1:2, probably modified by steric and electronic effects.

The triplet TMM could not be detected in control experiments of the direct photolysis. It was proposed that singlet TMM is formed, which can either cyclize to 6 or rotate to the orthogonal geometry and then cyclize to 7. These

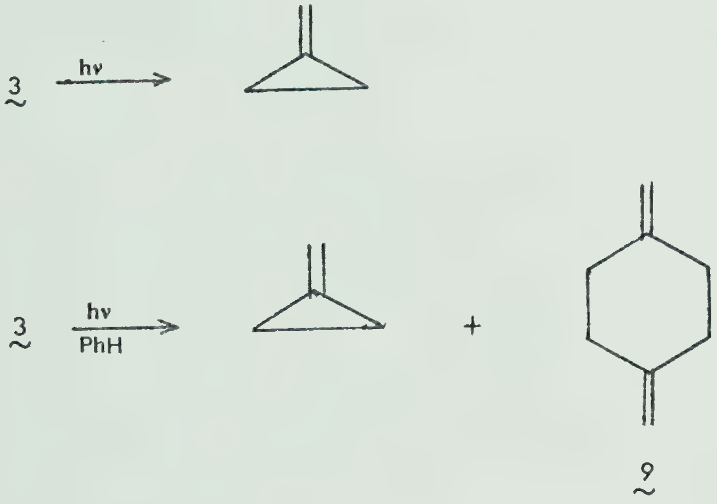
Table I

Photolysis of 4-Alkylidene-1-pyrazolines (**5a**,**5b**)

	Relative yields, %	
	6	**7**
Direct Photolysis		
5a	77	23
5b	64	36
Photosensitized Photolysis		
5a	25	75
5b	18	82

results have been confirmed by Sanjiki et al. in a very similar study (9).

Gajewski (10) observed analogous results. When 4-methylene-1-pyrazoline (3) was photolyzed directly, only

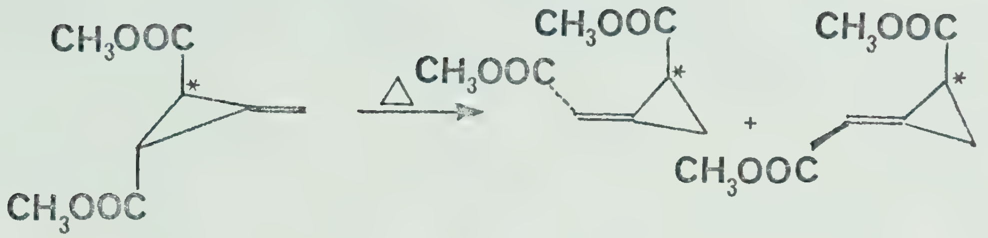


methylenecyclopropane was produced. But when photosensitized by benzene, 1,4-dimethylenecyclohexane (9) was also produced. The author proposes a singlet TMM intermediate for the direct photolysis, and singlet and triplet TMM for the photosensitized photolysis, with possibly singlet 3 intersystem crossing to triplet 3.

(B) TMM as an Intermediate in Thermolytic Rearrangements.

In 1960 Ullman (11) found that optically active *trans* Feist's ester (10) rearranged with retention of configuration in the mixture of products. This indicated that

an achiral intermediate cannot be involved.



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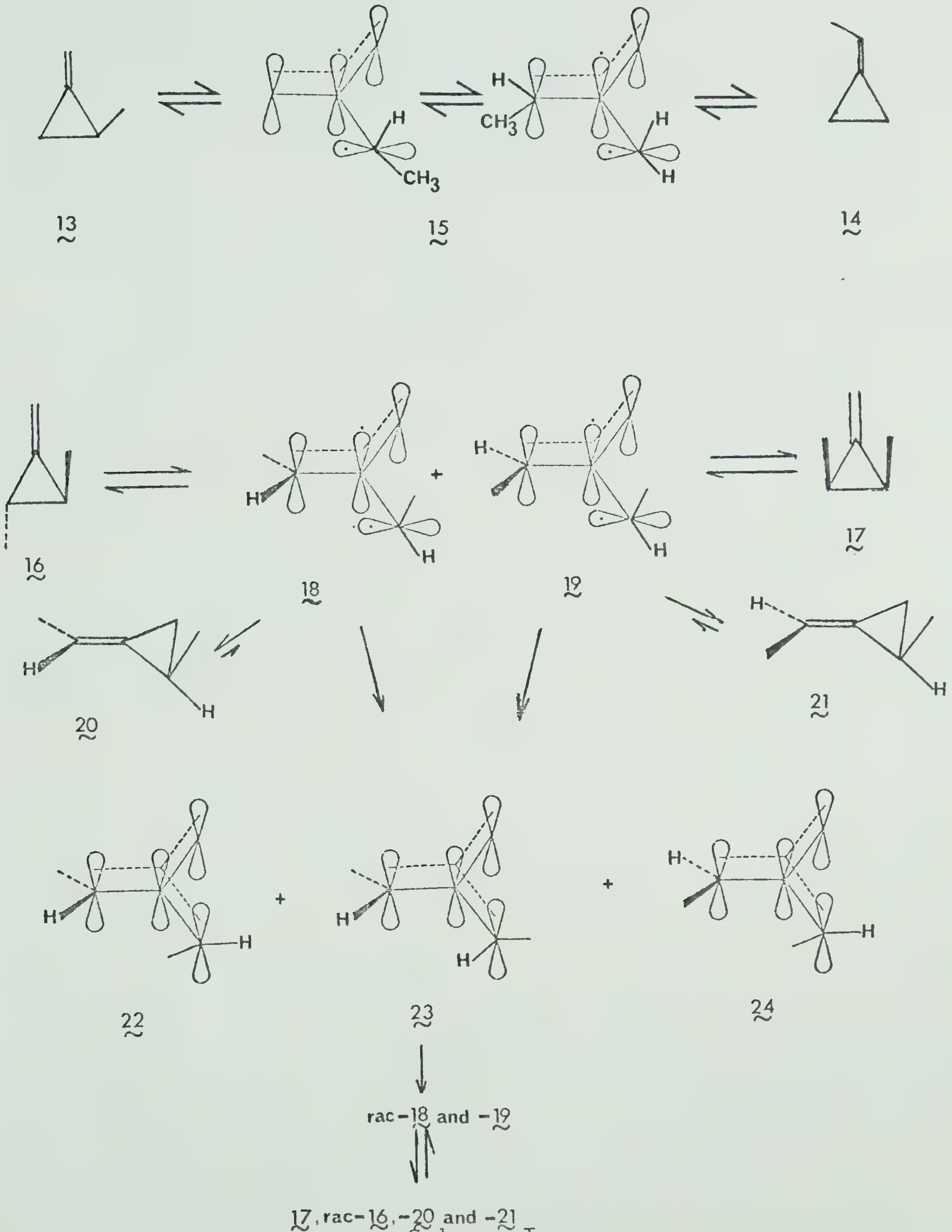
In a further study (11a) it was found that geometric isomerization was not confined to Feist's ester, but also took place in the analogous methylenecyclopropaneacetate, which after equilibration at 250° resulted in a 11:12 ratio of 42:58. The mechanisms were explained by a zwitterion intermediate.

11

12

Chesick (12) investigated the thermal interconversion of methylmethylenecyclopropane (13) and ethylidenecyclopropane (14) and concluded that the equilibration was achieved through an orthogonal TMM intermediate 15.

In an extension of Ullman's study, Gajewski (13) investigated the rearrangement of optically active *trans*-2,3-dimethylmethylenecyclopropane, Scheme I. After ther-

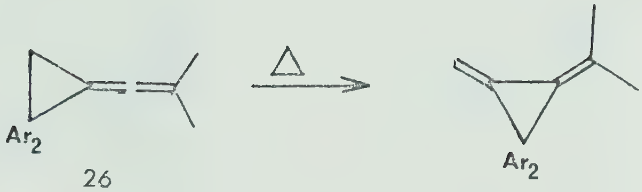

13
15
14
H
CH3
H
CH3
H
H
16
18
19
17
H
H
H
H
+
20
21
H
H
H
22
23
24
H
H
H
H
H
H
+
+
rac-18 and -19
17, rac-16, -20 and -21

Scheme I

molysis products **16**, **20** and **21** were found with predominant preservation of chirality. To account for the geometrical isomerization and predominant retention of optical activity, two chiral orthogonal TMM intermediates were invoked. However, a little racemization was found in **16**, **20** and **21**. This led Grajewski to assume that an achiral planar TMM was formed from the orthogonal one by a 90° rotation.

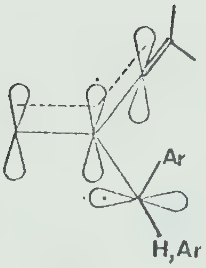
Doering (14), on the basis of Ullman's and Gajewski's studies, suggested a pivot mechanism in which one of the termini of TMM on opening of the ring rotates 90°. Thus a planar allylic radical is formed with a free radical attached to the center atom in a perpendicular and nonbonding arrangement. On examination of a number of compounds he decided that the pivot atom is the one which carries the better radical stabilizing groups. While this is not always true, as can be seen from Chesick's work, other studies with strongly radical-stabilizing groups confirm Doering's hypothesis, e.g. the study by Hendrick, Hardie and Jones (15) on the thermolysis of the monophenylalkenylidenecyclopropane (**25**) at 310° in the gas phase, and the diphenylalkenylidenecyclopropane (**26**) at 80° in carbon tetrachloride. The only products found had the phenyl substituents on the cyclopropane ring. This is best explained by the production of the free benzyl radical (**27**).

$\underset{\sim}{25}$



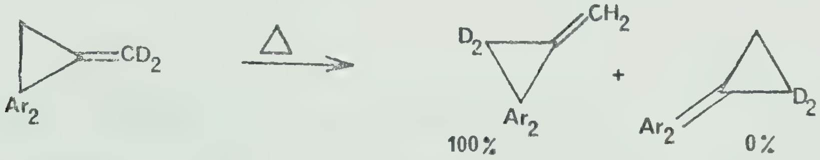
$\underset{\sim}{26}$

Ar = C_6H_5



$\underset{\sim}{27}$

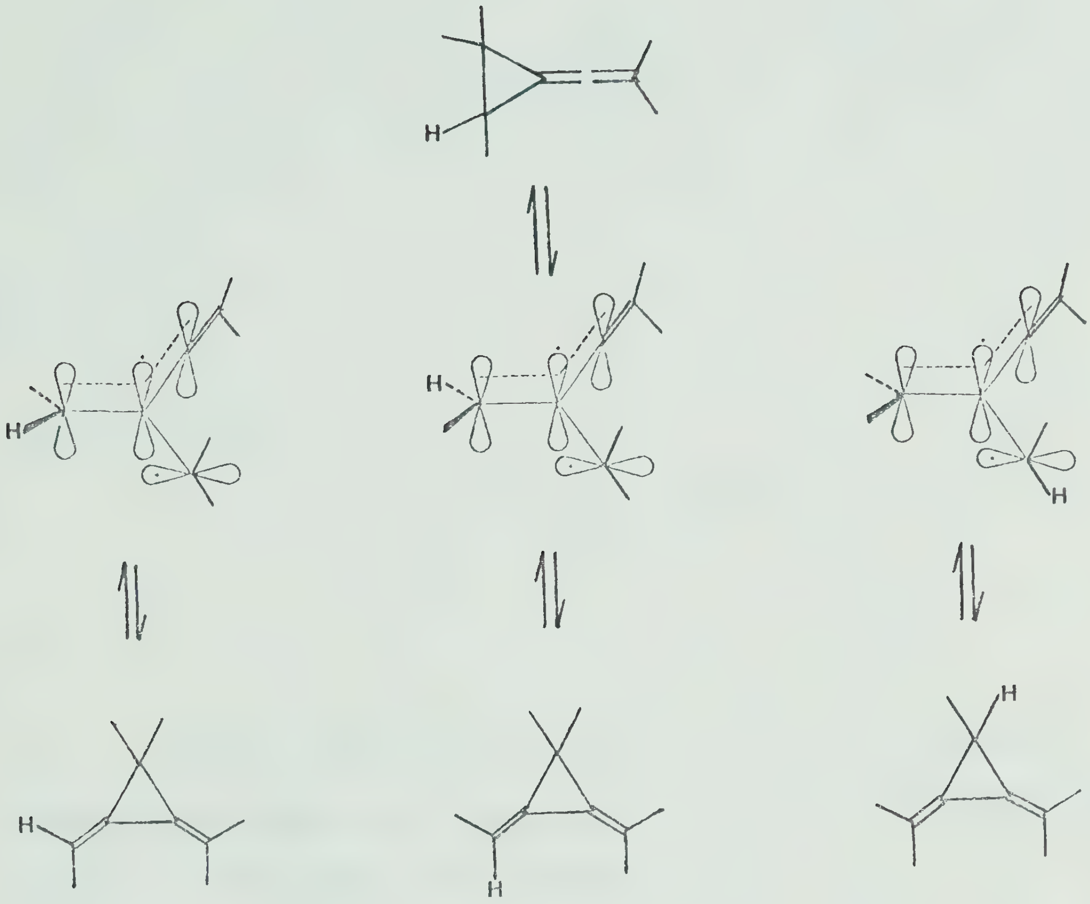
Analogous results were obtained by Gilbert and Butler (16) in thermolysis of 2,2-diphenyl-1-(dideuteriomethylene)-cyclopropane.



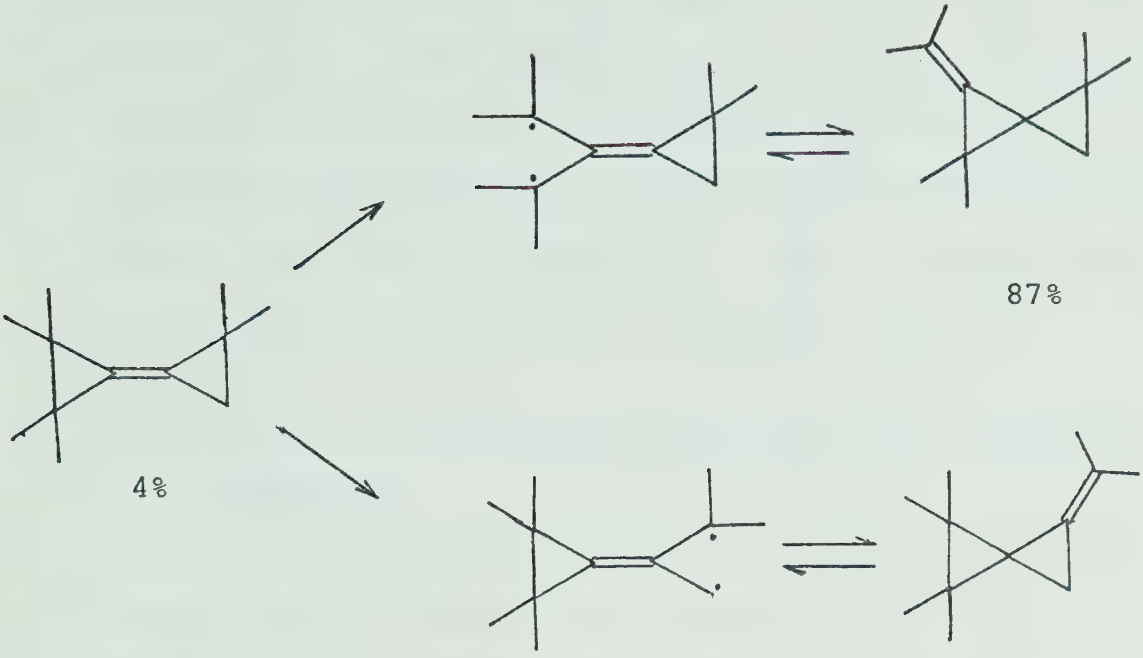
Ar = C_6H_5

Numerous other thermal rearrangements have been carried out and the intermediacy of TMM has been established.

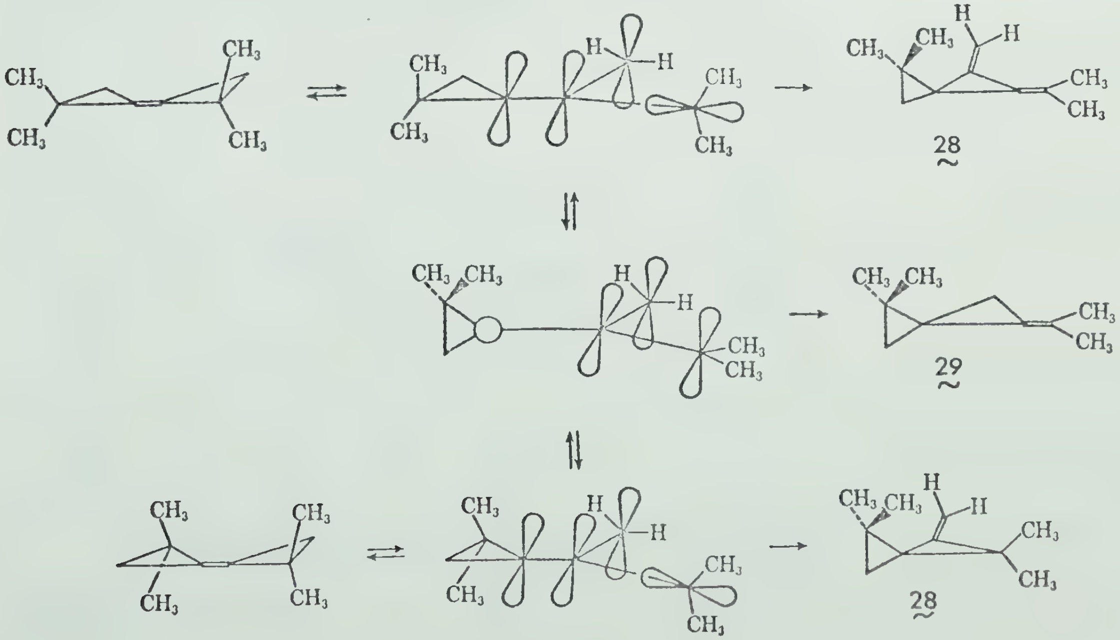
Crandall et al. (17) investigated the pyrolysis of 1-(2-methylpropenylidene)-2,2,3-trimethylcyclopropane in a flow system and found three isomeric hydrocarbon products, which can be explained by assuming three different orthogonal TMM intermediates.



In another study (17a) 2,2,3,3,2',2'-hexamethylbiscyclopropylidene was rearranged at 400° in a flow system to yield two methylenespiropentane products. The product distribution reflects the stabilization of the diradical intermediate and the relief of non-bonded interaction between the four methyl groups on the cyclopropane ring.



The thermolysis of *cis* and *trans*-tetramethylbiscyclopropylidene by Dolbier et al. (18) is also a good example of different TMM intermediates.



Product 28 was produced in large excess over 29. This agrees with the most stabilized free radical terminal being the pivot group which gives product 28 from both *cis* and *trans* starting material. A planar TMM intermediate would rather ring close to product 29, since a primary radical site is more reactive than a tertiary site.

(C) TMM as Intermediate in Thermolysis of 4-Methylene-1-pyrazolines.

Pyrolysis of 4-methylene-1-pyrazoline (3) has been carried out by Crawford and Cameron (5, 19). As mentioned before, a singlet TMM intermediate was produced.

In order to investigate the mechanism of this thermolysis the 4-methylene-1-pyrazoline-3,3-$\underline{d}_2$ (30) and 4-methylene-1-pyrazoline-3,3,6,6-$\underline{d}_4$ (31) were prepared and thermolyzed to give products 32 and 33, and 34 and 35, in relative yields as in Table II

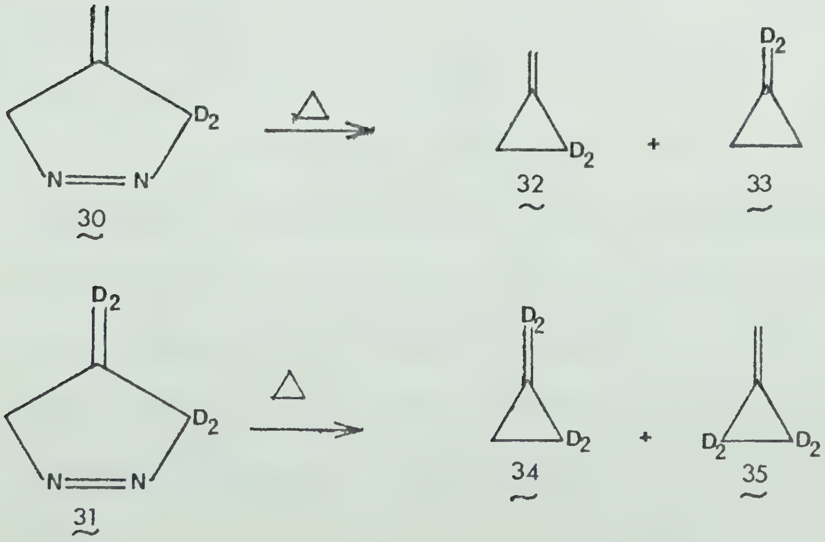


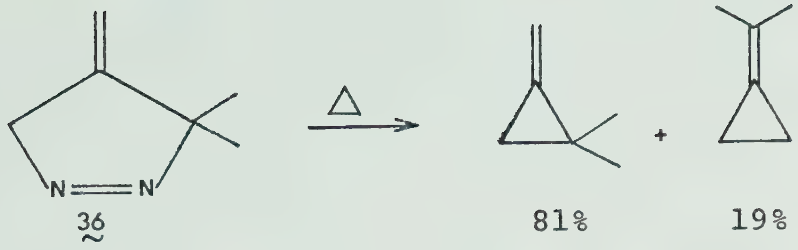
Table II

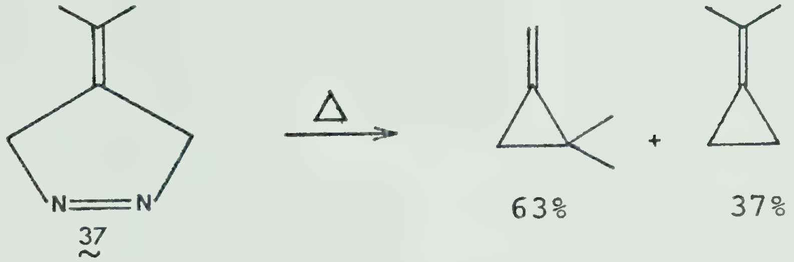
Thermolysis of Deuterated 4-Methylene-1-pyrazolines (**30**,**31**)

Starting Material	Relative Yields, %	
	32	**33**
30	59.3	40.7
	34	**35**
31	73.8	26.2

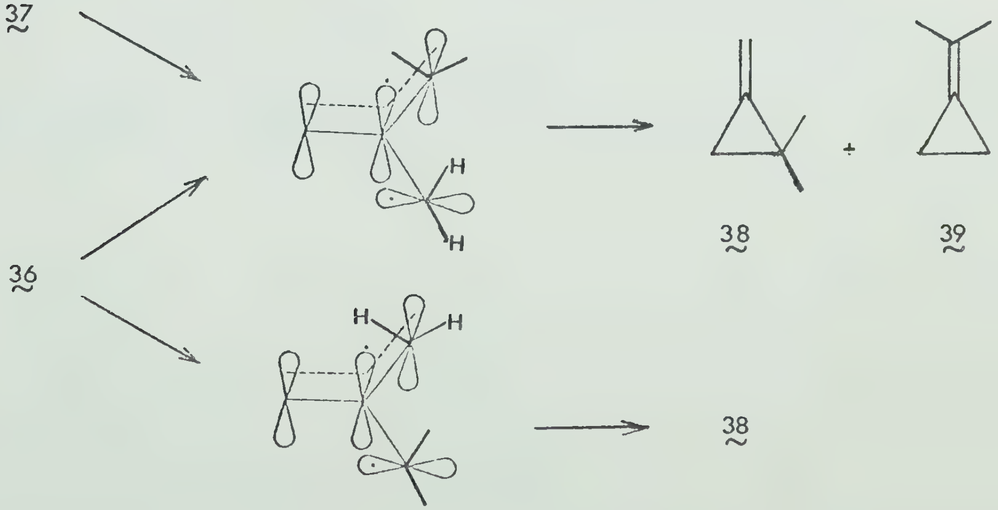
In the case of a planar TMM intermediate which would give the statistical distribution of 67:33 for products **32**:**33**, a secondary isotope effect could be calculated of $k_H/k_D = 1.37$ to explain the difference. When the same value was applied to correct the statistical distribution in the thermolysis of **31** a good fit was obtained with the observed distribution. This implies that a singlet TMM may be the intermediate in these thermolyses.

Tokunaga (20) investigated the thermolysis of two isomeric dimethyl substituted 4-methylene-1-pyrazolines (**36**) and (**37**) and obtained the indicated product distribution. The mechanism of this thermolysis could not be explained through a planar TMM intermediate, but fits the mechanism of an orthogonal TMM, Scheme II.





From this scheme it is apparent, that in the thermolysis of 36 the ratio of 38:39 should be increased relative to the product ratio from 37.



Scheme II

OBJECTIVE

The thermolysis of 4-methylene-1-pyrazoline (**3**) implies a planar TMM intermediate (5,19). On the other hand thermolysis of 3,3-dimethyl-4-methylene-1-pyrazoline (**36**) or 4-isopropylidene-1-pyrazoline (**37**) is best discussed in terms of an orthogonal TMM intermediate (20). These results cannot easily be reconciled, unless the substituents on TMM through their steric and electronic effects influence the otherwise non-substituted planar TMM to assume an orthogonal structure.

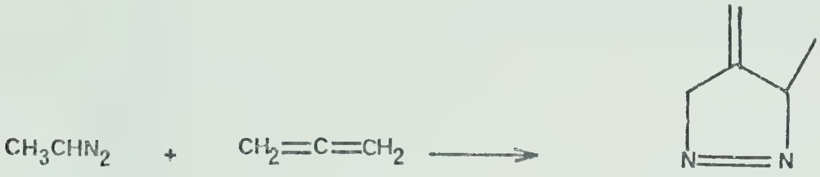
It is therefore interesting to examine the products of another isomeric pair of 4-methylene-1-pyrazolines, possibly a pair that would exhibit less steric and electronic changes than the dimethyl substituted pair of **36** and **37**. If the mechanism follows one of the earlier patterns then possibly some more general mechanistic trends can be ascertained.

The pair selected therefore was 3-methyl-4-methylene-1-pyrazoline and 4-ethylidene-1-pyrazoline.

RESULTS

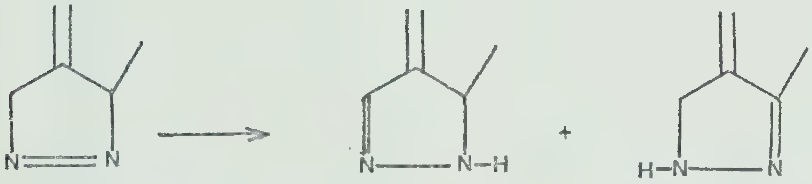
(A) Synthesis

3-Methyl-4-methylene-1-pyrazoline (40) was prepared from the addition of diazoethane to allene (19). The n.m.r. spectrum is shown in Figure 2.

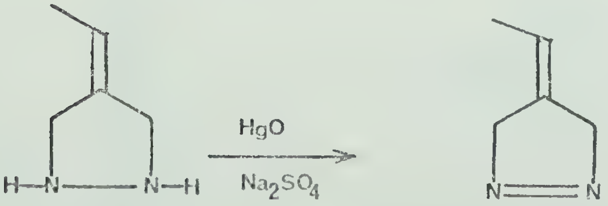


40

The compound 40 can be stored for more than four months at -20°, but, left at room temperature it tautomerizes to the two possible tautomeric 4-methylene-2-pyrazolines in a matter of days.



4-Ethylidene-1-pyrazoline (41) was obtained by mercuric oxide oxidation of the corresponding pyrazolidine (42),



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41

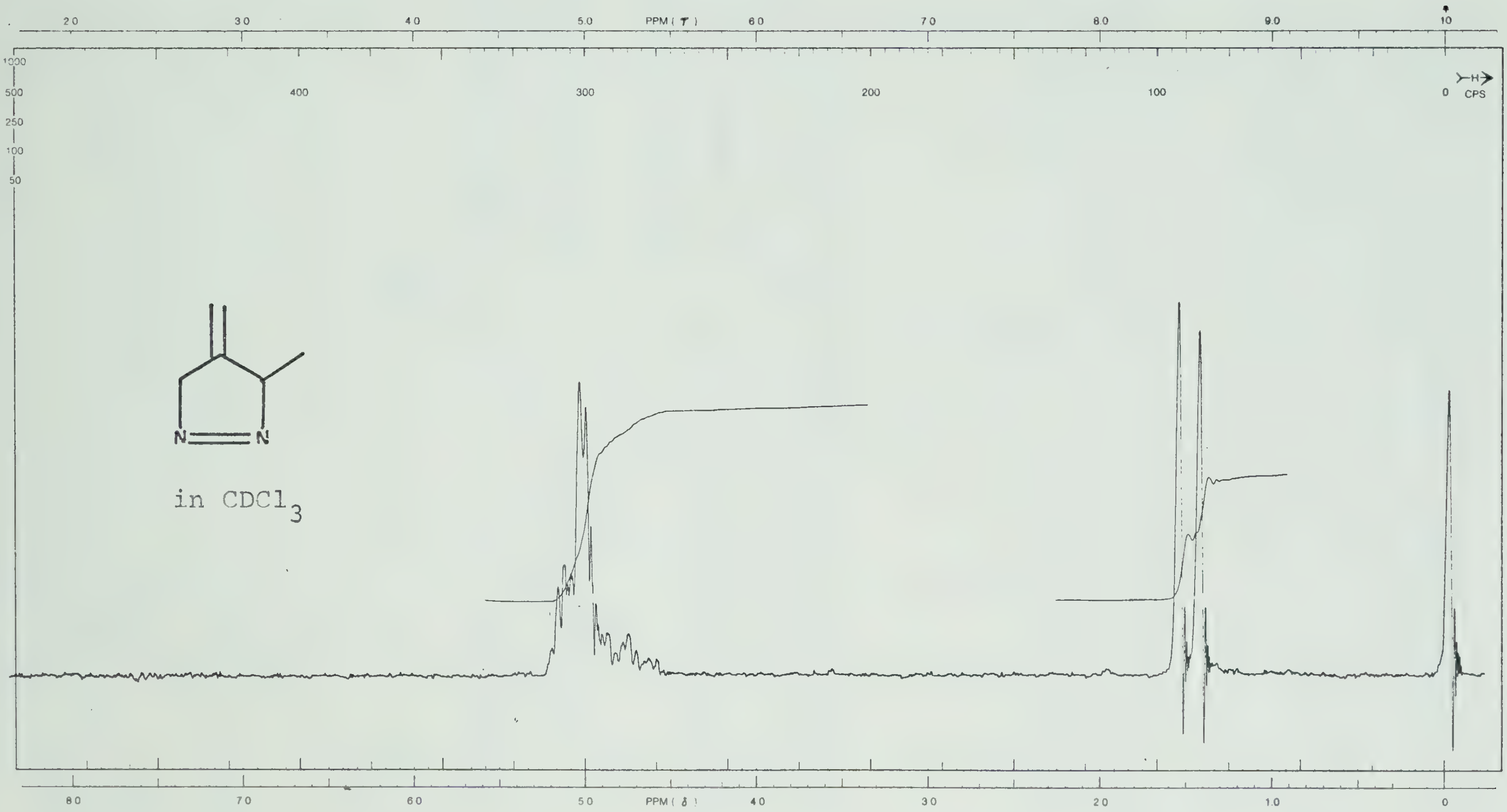
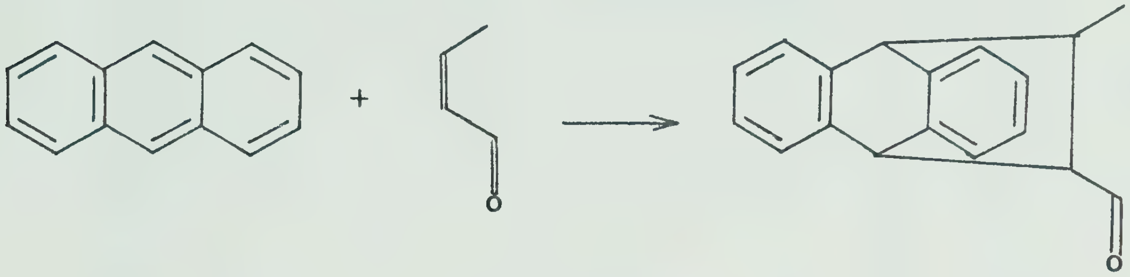


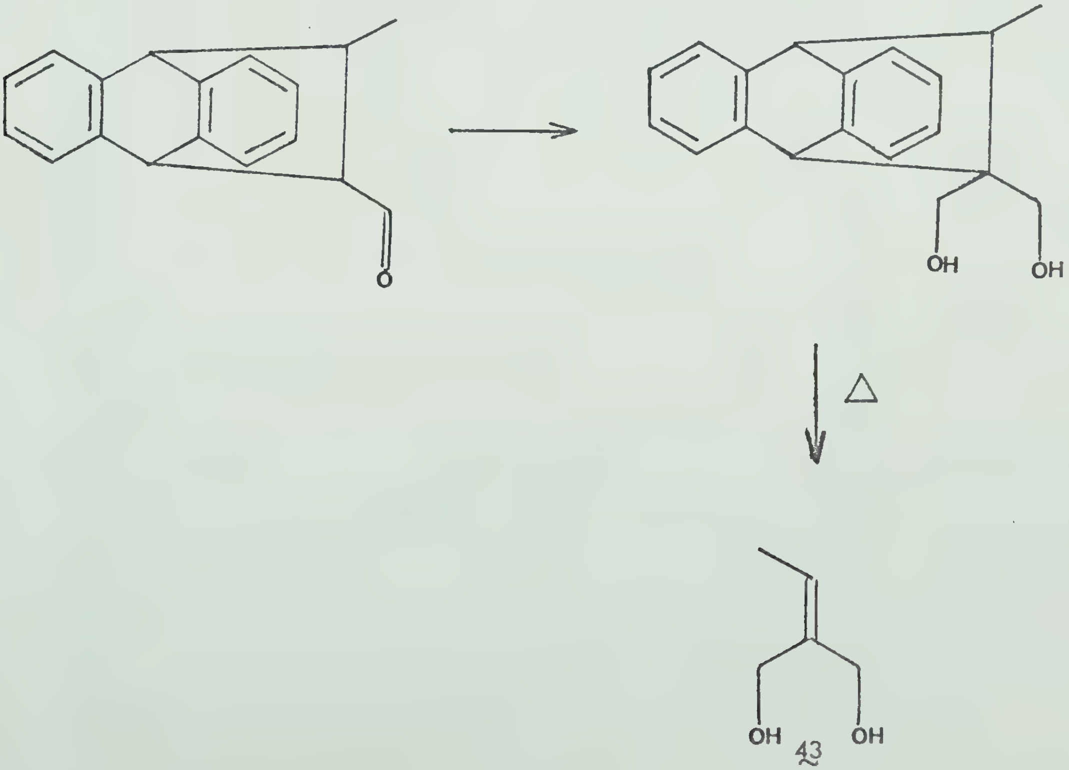
Figure 2. The nmr spectrum of 3-methyl-4-methylene-1-pyrazoline (40).

which in turn was obtained through a sequence of synthetic steps. The n.m.r. spectrum is shown in Figure 3.

A Diels-Alder adduct was formed from anthracene and crotonaldehyde in an autoclave at 200° (21).



In the next step formylation and a crossed-Cannizarro reaction were carried out at the same time by refluxing the Diels-Alder adduct with a three-fold excess of formaldehyde and potassium hydroxide.



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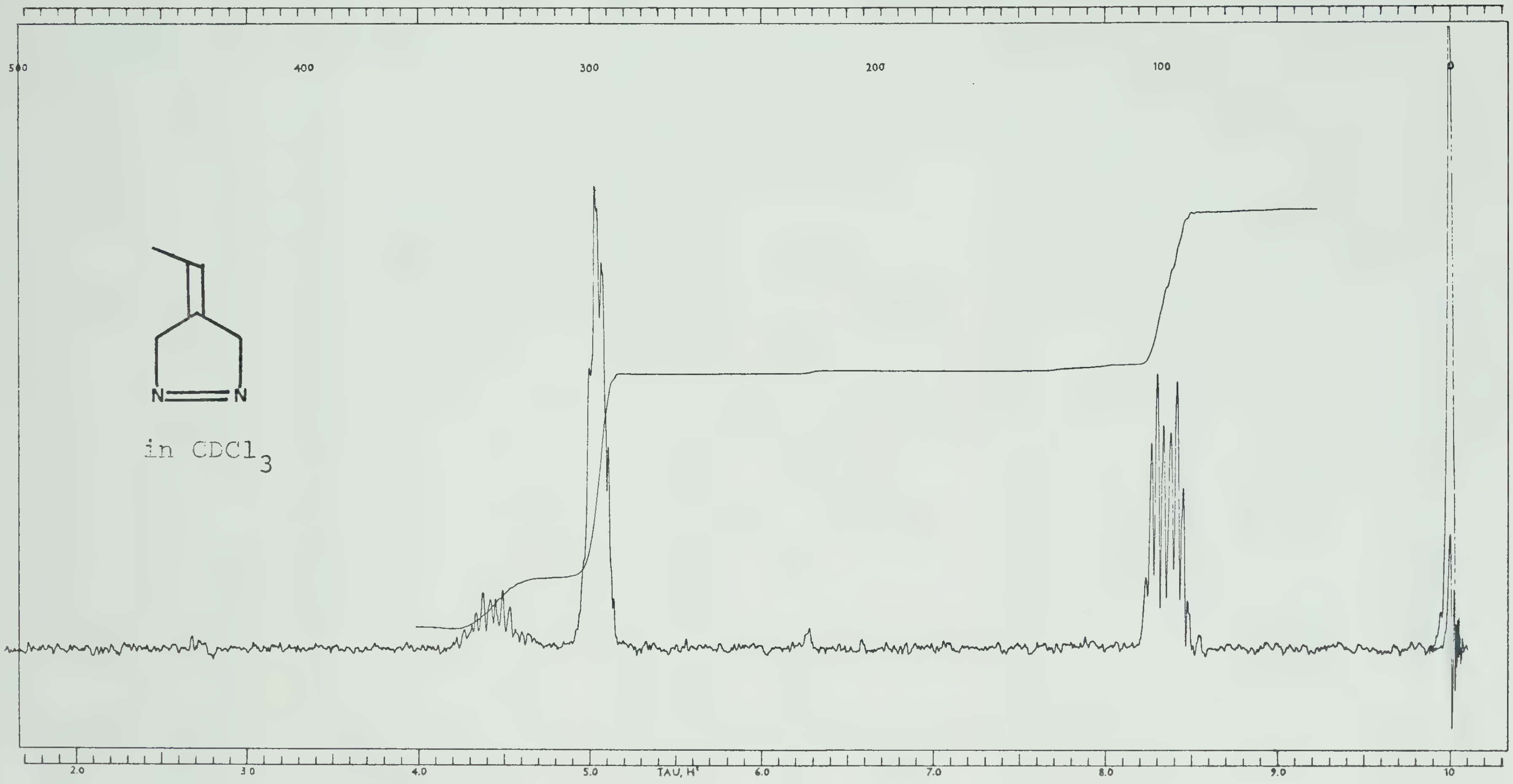
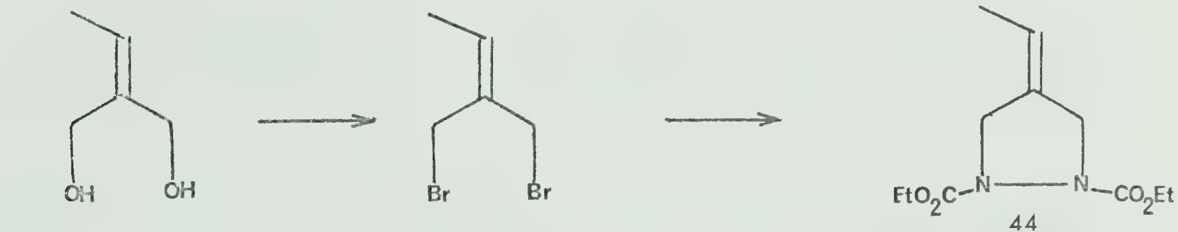


Figure 3. The nmr spectrum of 4-ethylidene-1-pyrazoline (41)

This was followed by a retro Diels-Alder reaction to produce the diol 43 which contains the basic hydrocarbon skeleton of the pyrazoline 41 (22).

Conversion of the diol 43 with phosphorus tribromide to the dibromide gave a low yield, since polymerization occurred easily. The dibromide, a very strong lachrymator, was then allowed to react with the dianion of diethyl-hydrazodicarboxylate (DEHD) to form the cyclic compound 44. Both the bromide and 44 were purified only once for analysis, but were otherwise used in a concentrated solution. A possible impurity could have been the isomeric



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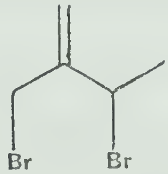

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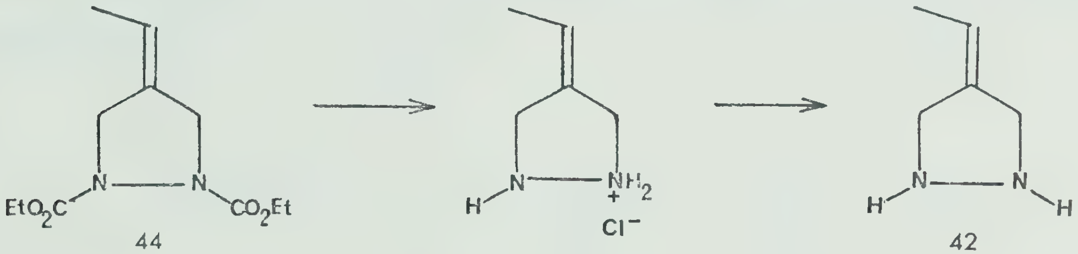
dibromide 45, but this was not detected during any of the syntheses.

The cyclic 1,2-dicarbethoxy-4-ethylidenepyrazolidine (44) was then hydrolyzed with potassium hydroxide in ethylene glycol by heating it at 120° overnight. The procedure was essentially that of Crawford and Al-Sader (23). Since the

pyrazolidine 42 is very soluble in water, a simple extraction with ether could not be carried out. Therefore the solution was distilled at reduced pressure until only solid potassium carbonate remained. Hydrochloric acid was then added to the distillate to produce the solid 4-ethylidenepyrazolidine hydrochloride and the remaining solution was evaporated off at reduced pressure (24).



44 42

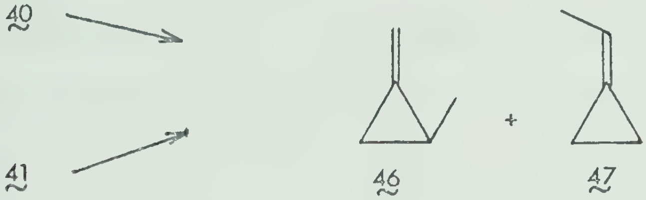
A thick oil of the pyrazolidine hydrochloride was obtained, probably as a consequence of some contaminating ethylene glycol. Continuous extraction with ether did not remove all of the ethylene glycol and the product was not further purified. The pyrazolidine hydrochloride was then neutralized with potassium hydroxide to produce the pyrazolidine 42, which was continuously extracted with ether and was not further purified. This solution was then oxidized by mercuric oxide to give 4-ethylidene-1-pyrazoline (41).

Pyrazoline (41) is less stable than 40. Left at room temperature a considerable amount of tautomerization, analogous to 40, takes place in a few hours to the two isomeric 4-ethylidene-2-pyrazolines. However, when 41 was stored

at -78° no tautomerization could be detected after one month.

(B) Thermolyses and Analysis of Products.

Thermolyses of the pyrazolines **40** and **41** were carried out in breakseals at about 580 torr at three different temperatures: 160°, 175° and 190°. The temperature of the oilbath was controlled to within ± 0.02°. The pyrazolines were thermolyzed for five different lengths of time at each temperature.



Since **46** and **47** slowly interconvert (12), initial conversion distribution could thus be calculated by extrapolation.

The products were analyzed by gc and the peak areas integrated by a Hewlett Packard 3370A electronic integrator.

In order to calculate the initial conversion product distribution the following formula for first-order kinetics was used (25).

$$\ln \frac{C_o - C_e}{C_t - C_e} = kt$$

If the concentration of **46** is equated to I and the formula is rearranged, it follows that:

$$\log (I_t - I_e) = k't + \log (I_o - I_e)$$

in which

$$k' = -\frac{k}{2.303},\ I_t = I \text{ at time } t,\ I_o = I \text{ at time } 0$$

and $I_e = I$ at equilibrium.

I_e was calculated by applying the formula (25):

$$R\ln K = \Delta S - \frac{\Delta H}{T} \quad \text{and}$$

$$K = \frac{II_e}{I_e},\ \text{with } \Delta S = -.55 \text{ eu},\ \Delta H = -.5 \pm .2 \text{ kcal/mole}$$

as reported by Chesick (12).

Plotting log $(I_t - I_e)$ versus time t, log $(I_o - I_e)$ can be obtained as the intercept at t = 0, and thus I_o can be calculated.

For each of the pyrazolines, **40** and **41**, at each temperature and length of time, three samples were examined. From each sample five gc analyses were made. Generally nine product distribution values were used to calculate each point. From the nine values the mean and the standard deviation were calculated. A sample calculation is shown in Table III and Figure 4 . For the other individual results see the Appendix. The slope and intercept of the line through the five time-points at each temperature was calculated by the least square method.

The error in the intercept was calculated by connecting the lower limit of one extreme point to the upper limit of the other extreme point and taking the two intercepts as the limits on the intercept found by the least square

Table III

Product Distribution of **40** Thermolysed at 190.12 ± .02°

Time (sec)	3600		1800		900		600		300	
Product (%)	**46**	**47**	**46**	**47**	**46**	**47**	**46**	**47**	**46**	**47**
	76.38	23.62	77.74	22.26	78.54	21.46	78.56	21.44	78.72	21.28
	76.69	23.31	77.25	22.75	79.22	20.78	78.72	21.28	78.81	21.19
	77.19	22.81	77.41	22.59	78.50	21.50	78.53	21.47	78.50	21.50
	76.39	23.61	77.84	22.16	77.79	22.21	78.73	21.27	78.41	21.59
	76.48	23.52	77.76	22.24	78.60	21.40	78.88	21.12	78.38	21.62
	76.92	23.08	77.55	22.45	78.41	21.59	78.39	21.61	78.92	21.08
	76.54	23.46	76.64	23.36	77.98	22.02	78.27	21.73	79.30	20.70
	77.18	22.82	77.40	22.60	78.76	21.24	77.94	22.06	79.46	20.54
	76.72	23.28	76.90	23.10	78.17	21.83	77.88	22.12	78.71	21.29
	76.97	23.03	76.93	23.07	79.03	20.97	78.40	21.60	79.23	20.77
	77.15	22.85	77.27	22.73	78.76	21.24	77.86	22.14	79.38	20.62
	76.24	23.76			78.41	21.59			78.28	21.72
	76.69	23.31			78.86	21.14			78.66	21.34
					78.56	21.44			78.61	21.39
									78.47	21.53
No. of analyses	13		11		14		11		15	
Mean	76.73	23.27	77.34	22.66	78.54	21.46	78.38	21.62	78.79	21.21
Standard Deviation	.33		.39		.39		.36		.39	

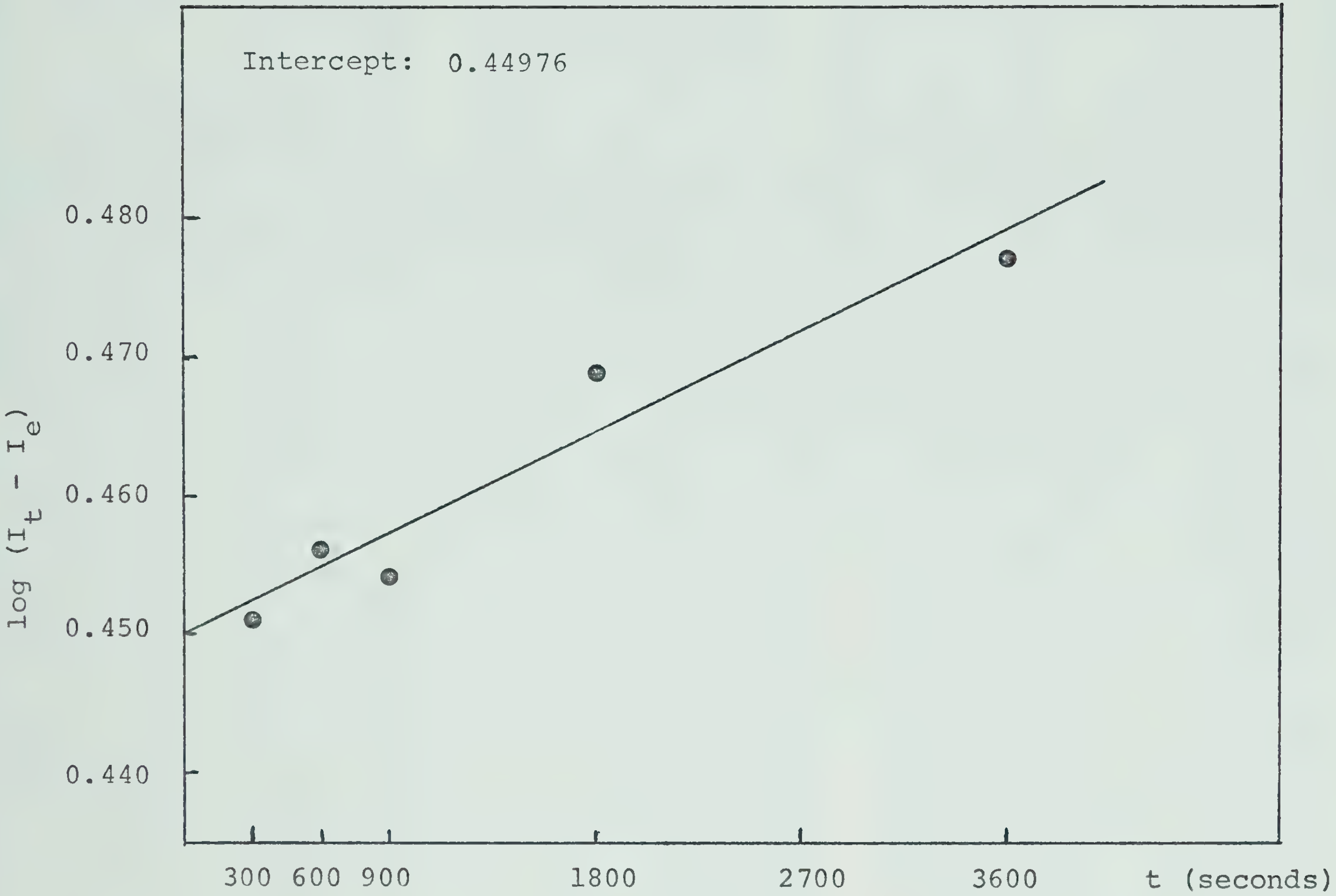


Figure 4. Graph of the Product Distribution versus Time of the Thermolysis of **40** at 190.12 ± .02°

method.

The zero conversion distributions of **46** and **47** are given in Table IV.

As can be seen from Table IV, variations of the temperature did not greatly affect the product distribution.

(C) Control Experiments

The two products were identified by taking an nmr spectrum of the mixture from thermolysis and analyzing the same mixture on gc. Enough peaks were resolved in the nmr spectrum to make assignment possible with the aid of the values reported by Chesick (12).

The possibility that excited methylenecyclopropanes **46** and **47** were formed, which could then equilibrate to both isomers, was examined. Thermolysis of **40** at 190° for one hour at three different pressures did not result in a significantly different product ratio (Table V). It thus appears that thermally excited methylenecyclopropanes were not formed.

An nmr spectrum (Figure 5) was taken of the total mixture at 55% conversion of **41**. It clearly demonstrates that:

(a) **41** was mainly converted to the products **46** and **47**

(b) **41** was slightly tautomerized to the two 4-ethylidene-2-pyrazolines.

(c) no interconversion of **41** to **40** could be detected

(d) no other hydrocarbon products could be detected.

An equilibration study of the products of thermolysis of **41** was carried out. The product ratio of **46**:**47** was

found to be 40:60, which is similar to the product ratio 44:56, calculated from Chesick's data (12).

Table IV

Product Distributions of 46 and 47 Produced from 40 and 41

Temperature	Starting with 40		Starting with 41	
	46	47	46	47
160.10°	80.64±.87	19.36±.87	89.96±.31	10.04±.31
175.06°	79.58±.61	20.42±.61	89.65±.58	10.36±.58
190.10°	78.88±.56	21.12±.56	89.43±.60	10.57±.60

Table V

Product Distributions of **46** and **47** from Thermolysis of **40** at 190° at Various Pressures

Pressure (torr)	Product ratio		
	46	:	**47**
330	76.55±.37		23.45±.37
450	76.88±.35		23.12±.35
690	76.73±.33		23.27±.33

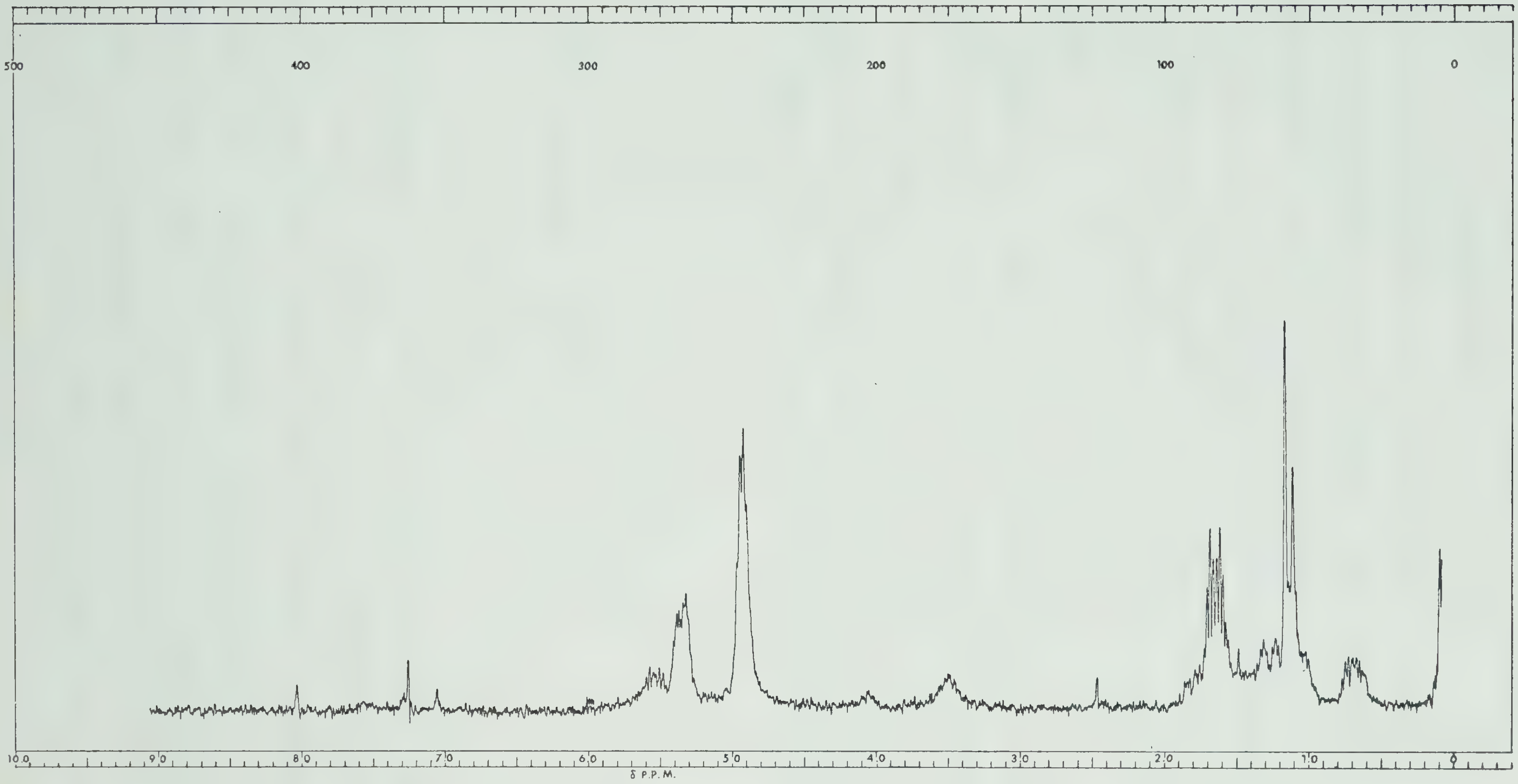


Figure 5. The 100 MHz nmr Spectrum of the Product Mixture at 55% Conversion of 41 (in $CDCl_3$).

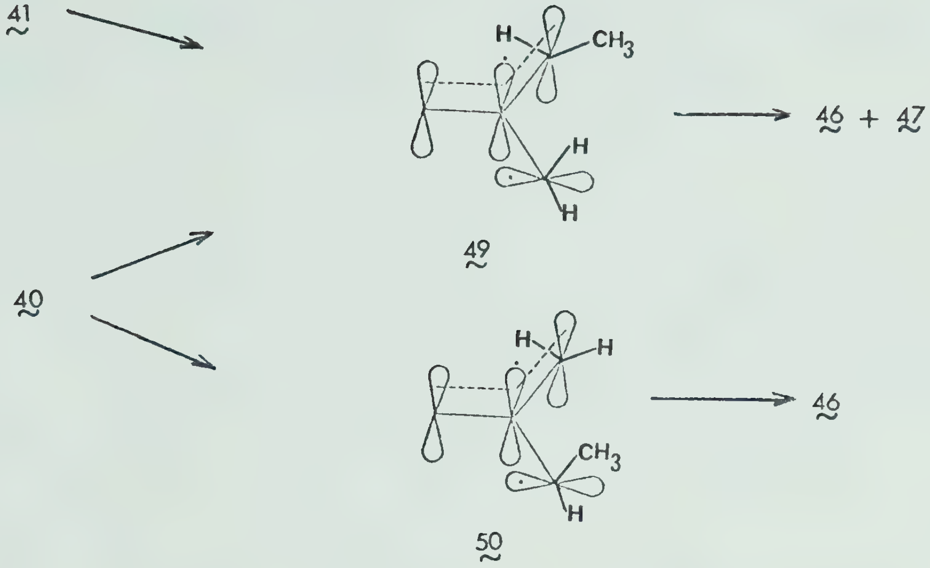
DISCUSSION

As outlined earlier the purpose of this work is to determine the proportions of the isomeric methylenecyclopropanes resulting from the thermolysis of 40 and 41. Comparison of these product proportions with those determined earlier from analogous substrates (5,20) may allow us to reconcile the mechanistic differences between the two previously studied systems.

In Cameron's work (5,19) it was possible to explain the product proportions in terms of a single TMM intermediate analogous to the planar species 48. If this is the case for 40 and 41, the ratio of 46:47 would be the same regardless of the reactant used. Table IV clearly demonstrates that such a single planar species as 48 does not explain the results.

48 46 47

The product proportions from the dimethyl-4-methylene-1-pyrazolines have been rationalized as proceeding through two intermediates (20). The analogous treatment of 40 and 41 would suggest that since 41 gives only the intermediate 49 and since it closes in the proportions of 8.66:1.00 (at 175°) to 46 and 47, then the relative amounts of 40 proceeding through



49 and **50** may be calculated since **47** only arises through **49***. Such a calculation suggests that 197% of **40** proceeds through **49**. This is clearly a ridiculous answer and thus the scheme that worked so well for the dimethyl-4-methylene-1-pyrazolines cannot apply to the monomethyl case, nor to the deuterio compounds.

Cameron (19) in speculating as to the mechanism of the methylenecyclopropane formation has suggested the possible intervention of a cyclopropyl radical in the mechanism. Such a radical would give with **40** and **41** the products **46** and **47**. This would predict that **41** would produce only **46** and that **40**

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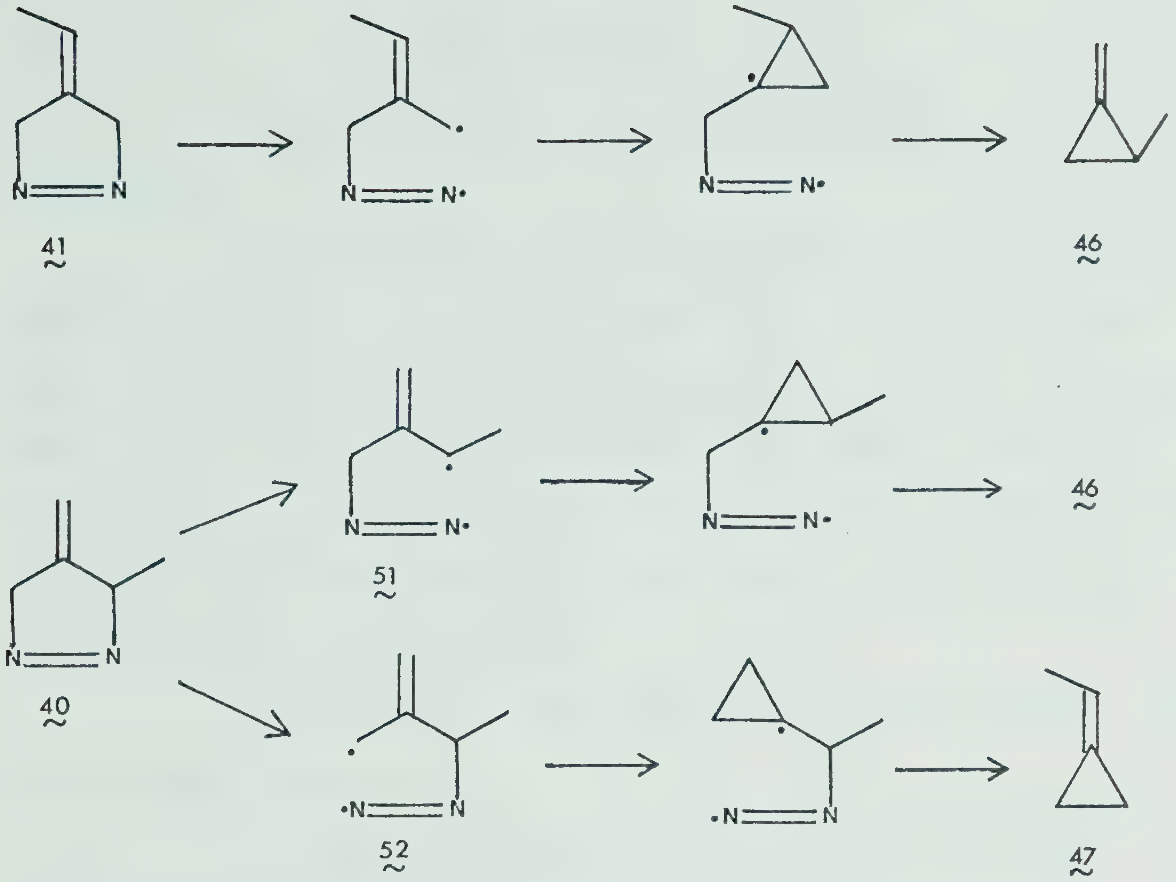
*The intermediate **49** may exist in isomeric *syn* and *anti* forms, but we have assumed that the reactivity of the methylene and the ethylidene groups in each form is comparable.



would produce a mixture of **46** and **47**. The possibility that the amount of **46** produced exceeds that of **47** is readily rationalized in terms of the greater ease of forming the methylallyl radical **51** than the allyl radical **52**. It is obvious that this mechanism while it most closely approximates the product proportions, is not capable of rationalizing the 10.5% of **47** produced from **41**.

It appears then that no single mechanistic pathway can reconcile the product distribution, and that further examples need to be examined in order to ascertain the factors controlling the product formation in the thermolysis of 4-methylene-1-pyrazolines.

EXPERIMENTAL

All boiling points and melting points are uncorrected.

Gas chromatographic analysis of the products were carried out on a Perkin Elmer Model 900 gc using a flame ionisation detector directly connected to a Hewlett Packard Model 3370 A electronic integrator and a Hewlett Packard Model 7127 A strip chart recorder. A 150 ft. capillary column with 0.01 inch inner diameter, wall coated with β,β'-oxydipropionitrile (ODPN) was used.

A Cary Model 15 spectrophotometer was used for the ultraviolet spectra.

The exact masses were determined on an A.E.I. MS-9 mass spectrometer.

Nuclear magnetic resonance spectra were obtained using a Varian A-60 spectrometer and a Varian Model HA-100 spectrometer.

Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, University of Alberta, Edmonton.

Oil Bath. The temperature of the oil bath, in which the product studies were carried out, was controlled by a Melabs proportional temperature controller Model CTC-1A and was measured by a Hewlett Packard Model 2801 A quartz thermometer. The probe (Serial No. S/N 974-21) was calibrated by the National Bureau of Standards. At 190° and 175° the value of 0.02 and at 160° 0.01 was added to the readings as those were the linearity corrections at those temperatures. During one run the temperature could be held constant within ± 0.01°; over the five runs at one temperature the temperature did not vary more than ± 0.02°.

Thermolyses. For every run three breakseals of ca 10 ml volume were filled with 10μl of neat pyrazoline by vapor transfer. The pressure inside the breakseals at the temperature of the runs was calculated to be ca 580 torr. After heating the breakseals were quickly quenched in ice-water. After the contents of the breakseals were vapor transferred to receivers, chloroform (30 μl) was added so as to prevent evaporation of the products.

Product Analysis. Gas chromatographic analyses were performed by injecting 0.3 - 0.4 μl of sample into an injection port which had a split ratio of 170:1. The 150 ft capillary ODPN column was held at 0° and the injection port at 50°.

The retention times were 5.5 min. for the 2-methyl methylenecyclopropane and 7.0 min. for the ethylidene cyclo-

propane.

For each sample five analysis were performed. If after the first peak the pen did not return completely to the baseline, the analytical data were rejected. After every five analyses the column was heated to remove chloroform, starting material and its tautomers.

Preparations. Ethyl N-nitroso-N-ethylcarbamate was prepared by the method of Hartman and Phillips (26), except that ethyl N-ethylcarbamate was substituted for ethyl N-methylcarbamate (27). The yield of the pink liquid was 203 g (74%). Bp. 52 - 53°/5 torr (lit. value 52.5 - 53.5°/5 torr (27)).

3-Methyl-4-methylene-1-pyrazoline (**40**). Diazoethane was prepared from ethyl N-nitroso-N-ethylcarbamate (25 g, 0.17 moles) according to the procedure of Wilds and Meader (27). The resulting solution of diazoethane in ether (ca 400 ml) was divided over four pressure bottles at 0°. Allene (ca 60 ml) was added to each bottle. The bottles were allowed to warm up slowly to room temperature overnight. Excess allene was allowed to evaporate from the colorless solutions. Ether was distilled off at atmospheric pressure through a Vigreux column. The residue was then distilled at reduced pressure. Bp. 37 - 38°/11 torr. Yield 1.5 g (9.2%). Nmr ($CDCl_3$) is shown in Figure 2. The uv spectrum showed λ_{max} = 326 mμ (ε = 488, methanol). Exact mass observed 96.0684, calculated for $C_5H_8N_2$ 96.0687.

Anal. Calcd. for $C_5H_8N_2$: C, 62.47; H, 8.39; N, 29.14

Found: C, 62.25; H, 8.46; N, 28.81

11-Formyl-12-methyl-9,10-dihydro-9,10-ethanoanthracene was prepared by the method of Weiss and Rusch (21). Anthracene (320 g, 1.8 moles), crotonaldehyde (155 ml, 1.65 moles), hydroquinone (1 g) and toluene (400 ml) were placed in a 1 ℓ autoclave and heated to 200 - 210° for 15 hrs. After cooling the mixture was filtered to remove unreacted anthracene. The filtrate was then concentrated on a rotary evaporator to remove toluene and unreacted crotonaldehyde. The residue was dissolved in ether (1 ℓ) and the precipitated anthracene was filtered off. The solution was again concentrated and set aside to cool off. On cooling it solidified. Yield 200 g (49.3%), mp. 98 - 100°.

11,11-Dihydroxymethyl-12-methyl-9,10-dihydro-9, 10-ethanoanthracene. The procedure was essentially that of Weiss and Bensa (22). 11-Formyl-12-methyl-9,10-dihydro-9, 10-ethanoanthracene (200 g, 0.807 moles), formaldehyde, 37% aqueous solution, (214 g, 2.64 moles), methanol (500 ml) and p-phenylenediamine (0.25 g) were placed in a 2 ℓ three-neck flask fitted with a mechanical stirrer and a reflux condenser. The apparatus was heated to 70 - 80°. Potassium hydroxide (47.5 g, 0.85 moles) was slowly added. The mixture was stirred for three hours at 70 - 80°. After cooling the precipitate was filtered off, washed with water and then with a

1:1 mixture of water and methanol. The solid was dried under vacuum over phosphorus pentoxide. Yield 171 g (75.6%), mp. 206 - 207°. Exact mass observed 280.1457, calcd. for $C_{19}H_{20}O_2$ 280.1463. Nmr (DMSO-d_6) δ 0.7 d(3H), 1.5 m(1H), 2.4 - 3.4 complex m (5H, should be 4H), 3.9 d(1H), 4.2 s(1H), 6.9 - 7.4 m(8H).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 81.39; H, 7.19

Found : C, 81.36; H, 7.08

2-Hydroxymethyl-2-buten-1-ol (**43**). The procedure was essentially that of Weiss and Bensa (**22**). 11,11-Dihydroxymethyl-12-methyl-9,10-dihydro-9,10-ethanoanthracene (88 g, 0.315 moles) was placed in a 100 ml flask fitted for distillation. The flask was heated to 280 - 330° for about one hour during which the glycol (**43**) and anthracene distilled off. The distillate was taken up in ether and the undissolved anthracene was filtered off. The filtrate was concentrated on a rotary evaporator and a further batch of anthracene was removed. The residue was distilled at reduced pressure. Bp. 105 - 108°/4.5 torr (Lit. value 110 - 113°/2 - 3 torr(22)). Yield 16.7 g (52%). Exact mass found 84.0576 (parent-H_2O), calcd. for $C_5H_{10}O_2$-H_2O 84.0575. Nmr ($CDCl_3$) τ 8.3 d(3H), 5.8 d(4H), 4.4 q(1H), 4.2 s(2H).

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.80; H, 9.87

Found : C, 59.07; H, 9.59

2-Bromomethyl-1-bromo-2-butene. 2-Hydroxymethyl-

2-buten-1-ol (45.5 g, 0.45 moles) dry pyridine (27.5 ml. 0.34 moles) and 450 ml 1:3 dry hexane-ether mixture were placed in a 1 ℓ three-neck flask fitted with a reflux condenser, nitrogen inlet, dropping funnel and mechanical stirrer. The flask was cooled in a dry ice-acetone bath and kept at -40 to -25° during the addition of phosphorus tribromide (38 ml. 0.40 moles) over about five hours. The mixture was then stirred for an additional two hours at -5°, after which it was poured onto 350 ml iced bicarbonate solution. The organic layer was separated and the water layer extracted three times with 500 ml hexane. The combined extracts were washed with water and dried over magnesium sulfate. The drying agent was filtered off and the solvent was distilled off through a Vigreux column. The residue was distilled at reduced pressure. Bp. 65 - 67°/4.5 torr. Yield of the very strong lachrymator 16.0 g (17.5%). Nmr ($CDCl_3$) τ 8.2 d(3H), 5.9 s(4H), 4.1 q(1H). Exact mass found 226.8999, calcd. for $C_5H_8{}^{79}Br_2$ 226.8982.

Anal. Calcd. for $C_5H_8Br_2$: C, 26.35; H, 3.54

Found: C, 26.33; H, 3.41

1,2-Dicarbethoxy-4-ethylidenepyrazolidine (44). *Sym*-Dicarbethoxyhydrazine (13.2 g, 0.075 moles) and 300 ml 1,2-dimethoxyethane (DME) (freshly distilled from lithium aluminum hydride) were placed in a 1 ℓ three-neck flask fitted with a reflux condenser, nitrogen inlet, magnetic stirrer and a dropping funnel. 57% Sodium hydride suspension (3.37 g, 0.08 moles sodium hydride) was added in small portions

and the mixture was stirred under nitrogen for five hours at room temperature. 2-Bromomethyl-1-bromo-2-butene (16.0 g, 0.07 moles) in 50 ml dry freshly distilled DME was added slowly over a period of four hours. The mixture was stirred for 40 hrs. Sodium ethoxide (0.075 moles, prepared from 1.7 g sodium in 50 ml absolute ethanol) was then added to the mixture, which was stirred for another 24 hrs. The mixture was concentrated on a rotary evaporator, so that all ethanol and DME was removed. The residue was poured onto 1000 ml ice and water and extracted with 500 ml ether. The combined extracts were dried over magnesium sulfate and the ether was removed on the rotary evaporator. The residue was distilled at reduced pressure. Bp. 130 - 134°/0.8 torr. Yield 5.7 g (33.7%). Exact mass found 242.1273, calcd. for $C_{11}H_{18}N_2O_4$ 242.1267. Nmr ($CDCl_3$) τ 8.75 t(7.5H), 8.4 d with fine splitting (3H), 5.8 distorted q(8H), 4.5 m(1H). The high integration at τ 8.75 (7.5H instead of 6H) is most likely caused by contamination by the oil of the NaH suspension.

Anal. Calcd. for $C_{11}H_{18}N_2O_4$: C, 54.53; H, 7.49; N, 11.56

Found : C, 55.31; H, 7.87; N, 10.96

That the analysis of C and H is too high, is also probably caused by contamination with oil.

<u>4-Ethylidenepyrazolidine hydrochloride</u>. 1,2-Dicarbethoxy-4-ethylidenepyrazolidine (19.0 g, 0.0785 moles), potassium hydroxide (35 g, 0.625 moles), ethylene glycol

(150 ml), and water (35 ml) were placed in a 500 ml flask fitted with a reflux condenser and nitrogen inlet. The reaction mixture was stirred and heated at 110 - 120° for 16 hrs. The mixture was then distilled under reduced pressure until only a solid residue was left (ca 100°/2 torr). The distillate was trapped in a receiver cooled by a dry ice-acetone bath. Cold concentrated hydrochloric acid (8.3 ml, 0.1 mole) was added to the distillate and the solvent was removed under reduced pressure. After almost all of the solvent had distilled off, the residue was placed in a vacuum desiccator with phosphorus pentoxide. Drying overnight did not give a solid and nmr showed ethylene glycol still present. The oily product was then dissolved in water and continuously extracted with ether for 24 hours. After removing the ether layer, the water layer was concentrated under vacuum until no more water distilled over. On cooling and drying the residue became a very thick oil. Yield 7.0 g (66.3%). Nmr (D_2O) τ 8.3 m(3H), 6.1 s(4H), 4.3 m(1H); it also showed ca 5.5% ethylene glycol present. The product was not further purified.

4-Ethylidenepyrazolidine (**42**). 4-Ethylidenepyrazolidine hydrochloride (9.0 g, 0.060 moles) was dissolved in water (50 ml) with stirring and was cooled by an ice bath. A solution of potassium hydroxide (6.70 g, 0.12 moles) in water (50 ml) was added. The mixture, under nitrogen, was extracted continuously with ether for two days. The ether solution was then dried and concentrated to about 100 ml by distillation

through a Vigreux column. The residue was distilled at reduced pressure. The pyrazolidine distills at ca 50°/2.5 torr, and was not further purified.

4-Ethylidene-1-pyrazoline. (41). In a 500 ml flask fitted with a dropping funnel, reflux condenser, nitrogen inlet, and magnetic stirrer, was placed red mercuric oxide (40 g), anhydrous sodium sulfate (40 g), and dry ether (100 ml). The slurry was well stirred and cooled in an ice-water bath. A solution of the pyrazolidine in ether was added dropwise over half an hour and the mixture was stirred at 0° for another three hours, after which it was stirred at room temperature overnight. The solids were filtered off and the ether of the filtrate carefully removed by distillation. The residue was distilled at reduced pressure. With the bath not higher than 60° some pyrazoline distilled over at 44 - 45°/10 torr, after which the pressure was reduced to 3 torr in order to transfer more of the pyrazoline. A redistillation at 3 torr with the oil bath at 55° gave the pure pyrazoline. Yield 1.25 g (21.7%, based on 4-ethylidenepyrazolidine hydrochloride). Exact mass found 96.0687, calcd. for $C_5H_8N_2$ 96.0688. The uv spectrum showed λ_{max} = 320 mμ, (ε = 523, methanol). The nmr spectrum in $CDCl_3$ is shown in Figure 3.

Anal. Calcd. for $C_5H_8N_2$: C, 62.47; H, 8.39; N, 29.14

Found: C, 62.49; H, 8.65; N, 29.03

Control Experiments. Product identification was obtained by

thermolyzing 100 µl of **40** at 190° for one hour and taking an nmr spectrum of the mixture of the products. The same sample was analyzed by gc, which indicated a 76:24 product ratio for **46** and **47**. Nmr showed also a 75:25 ratio of the two isomeric methylenecyclopropanes **46** and **47**, on the basis of two resolved peaks of each:

nmr ($CDCl_3$) **46**: τ 9.3 m(1H), 8.6 - 9.0 m and d, 4.6 m(2H)
47: τ 8.6 - 9.0 m, 8.15 d with fine splitting (3H), 4.15 m(1H)

A pressure dependency study was carried out by thermolyzing **40** at 190° at different initial pressures. The product distribution observed is in Table V, which indicates that there is no significant variation with pressure.

Pyrazoline **41** was thermolyzed at 160.25° for 10 min. Care was taken to transfer all products completely to a sample tube and an nmr was taken. It was found that 55% of **41** had converted. 45% was identified as methylenecyclopropane **46**, 5% was identified as **47** and 5% as the tautomeric 2-pyrazolines. No other peaks could be detected, such as peaks of **40**. The nmr spectrum is shown in Figure 5.

Pyrazoline **41** was thermolyzed at 211.79° for more than 12 half lives to check the equilibrium distribution against the value calculated by Chesick's data (12). The observed ratio of **46**:**47** was 40:60, calculated was 44:56.

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VITA

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In 1970 he married Coby Zeeman and is a father of one girl.

Appendix

Individual results of the product studies of 3-methyl-4-methylene-1-pyrazoline (**40**) and 4-ethylidene-1-pyrazoline (**41**).

Table A-1

Product Distribution of **40** Thermolyzed at 175.06±.02°

Time (sec)	3600		2700		1800		900		600	
Product (%)	**46**	**47**	**46**	**47**	**46**	**47**	**46**	**47**	**46**	**47**
	78.66	21.34	79.10	20.90	78.90	21.10	79.32	20.68	80.47	19.53
	78.74	21.26	78.55	21.45	79.07	20.93	79.83	20.17	79.55	20.45
	78.68	21.32	78.92	21.08	78.89	21.11	79.94	20.06	78.75	21.25
	78.74	21.26	78.16	21.84	79.30	20.70	79.28	20.72	79.37	20.63
	78.50	21.50	78.78	21.22	78.80	21.20	79.38	20.62	79.29	20.71
	78.53	21.47	78.09	21.91	79.15	20.85	79.65	20.35	79.23	20.77
	78.96	21.04	78.51	21.49	78.64	21.36	78.98	21.02	79.23	20.77
	78.81	21.19			78.69	21.31			79.24	20.76
	78.80	21.20			78.69	21.31			79.01	20.99
	78.41	21.59			78.48	21.52			79.30	20.70
					79.36	20.64			79.22	20.78
No. of Analyses	10		7		11		7		11	
Mean	78.68	21.32	78.59	21.41	78.91	21.09	79.48	20.52	79.38	20.62
Standard Deviation	.17		.38		.28		.34		.44	

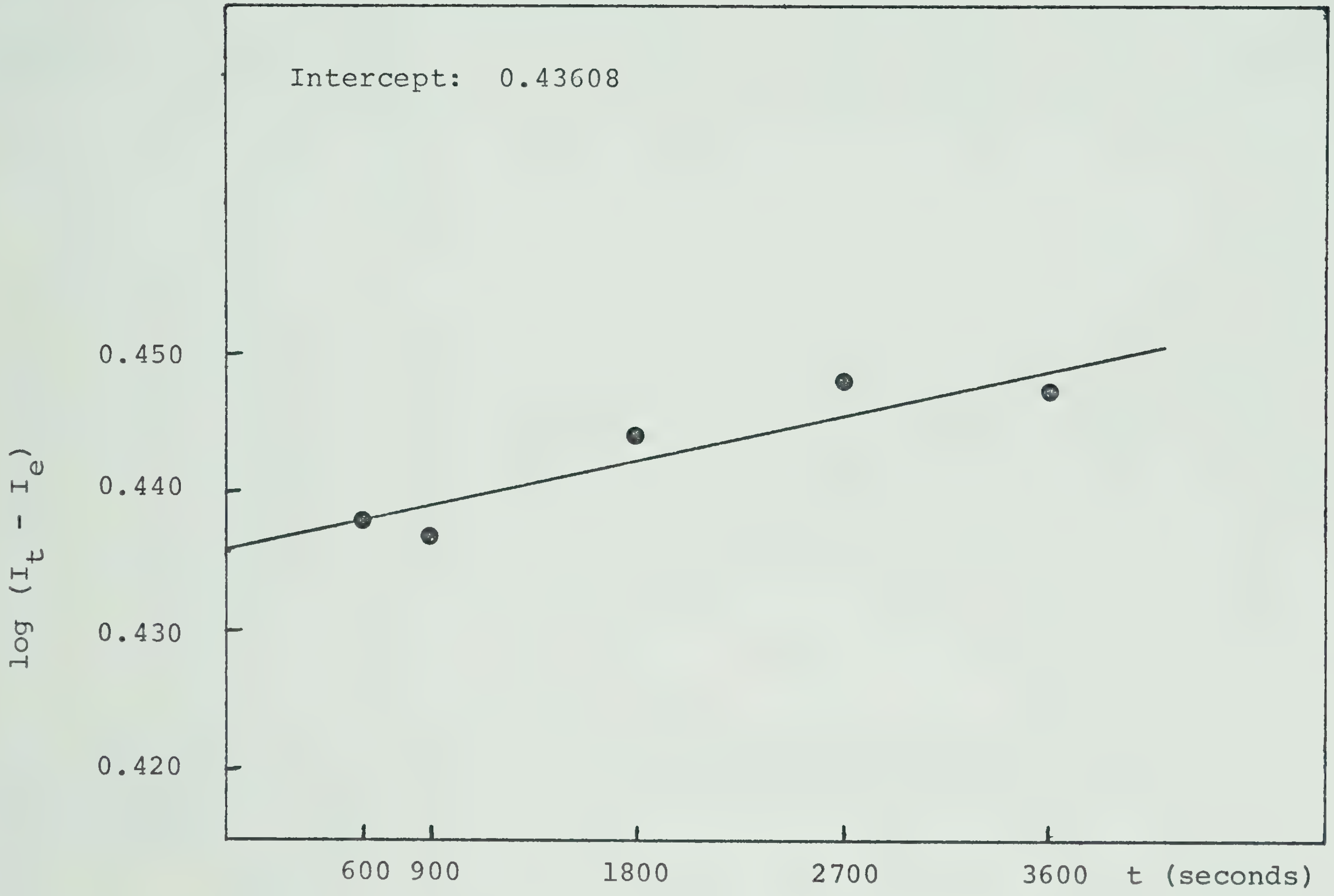

Figure A-1. Plot of Product Distribution versus Thermolysis Time of **40** at 175.06±.02° (see RESULTS, page 24).

Table A-2

Product Distribution of **40** Thermolyzed at 160.10±.02°

Time (sec)	3600		2700		1800		900		600	
Product (%)	**46**	**47**	**46**	**47**	**46**	**47**	**46**	**47**	**46**	**47**
	80.65	19.35	79.65	20.35	79.45	20.55	81.09	18.91	81.49	18.51
	80.38	19.62	79.87	20.13	79.86	20.14	80.86	19.14	80.94	19.06
	80.08	19.92	80.29	19.71	79.88	20.12	80.51	19.49	81.43	18.57
	80.07	19.93	79.46	20.54	80.45	19.55	80.63	19.37	80.62	19.38
	79.87	20.13	80.45	19.55	80.45	19.55	80.35	19.65	80.33	19.67
	80.17	19.83	80.34	19.66	79.95	20.05	80.54	19.46	80.61	19.39
	80.04	19.96	79.51	20.49	80.16	19.84	80.64	19.36	80.78	19.22
	80.33	19.67	79.92	20.08	79.52	20.48	80.17	19.83	80.31	19.69
			80.35	19.65			80.78	19.22	79.81	20.19
							80.26	19.74		
							80.31	19.69		
No. of analyses	8		9		8		11		9	
Mean	80.20	19.80	79.98	20.02	79.97	20.03	80.56	19.44	80.70	19.30
Standard Deviation	.24		.39		.38		.28		.54	

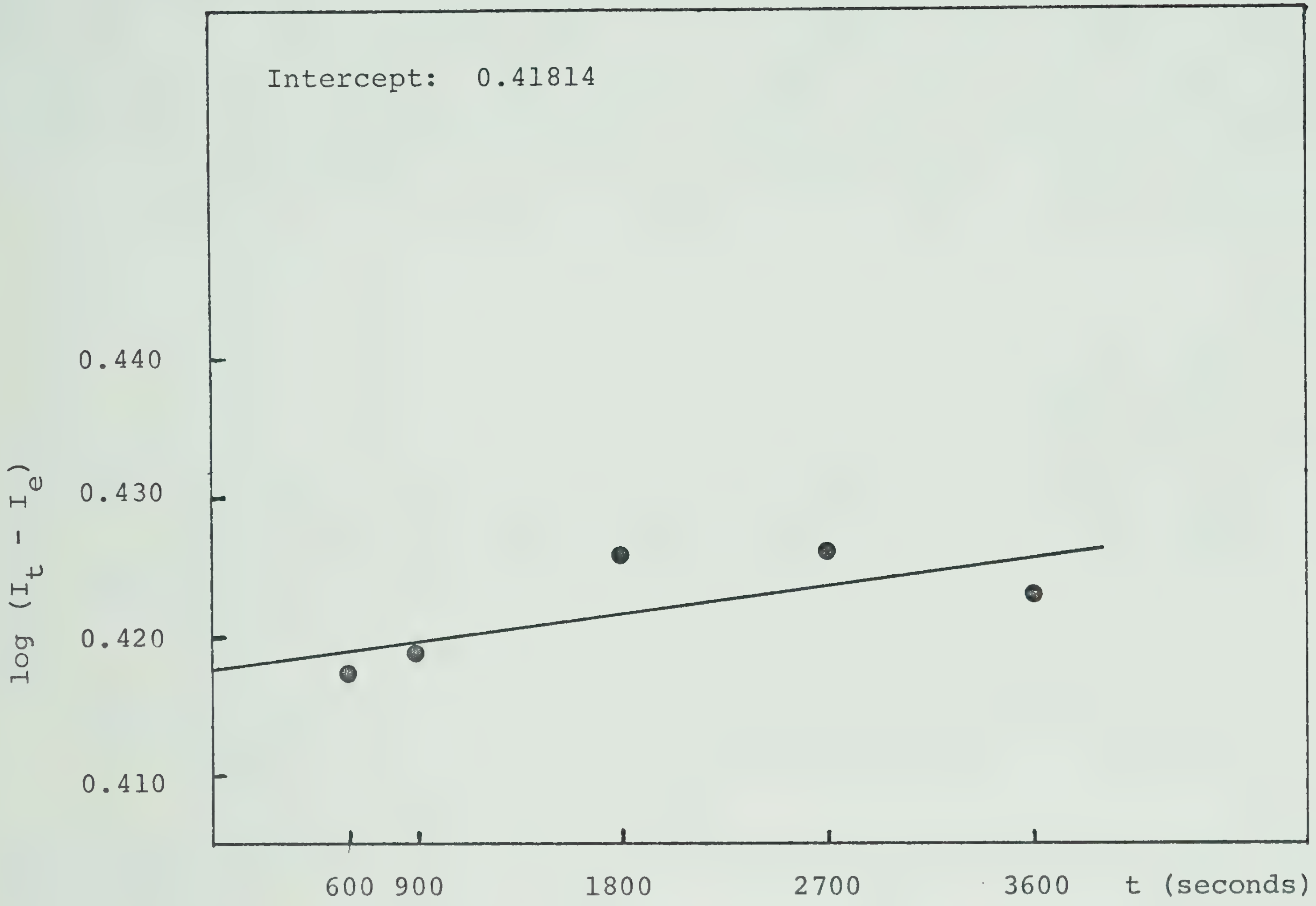

Figure A-2. Plot of Product Distribution versus Thermolysis Time of **40** at 160.10±.02° (see RESULTS, page 24).

Table A-3

Product Distribution of **41** Thermolyzed at 190.12±0.2°

Time (sec)	3600		2700		1800		900	
Product (%)	**46**	**47**	**46**	**47**	**46**	**47**	**46**	**47**
	86.81	13.19	87.55	12.45	87.94	12.06	88.45	11.55
	86.42	13.58	87.81	12.19	88.27	11.73	88.93	11.07
	86.53	13.47	87.28	12.72	88.14	11.86	88.72	11.28
	86.32	13.68	87.71	12.29	88.08	11.92	88.59	11.41
	86.41	13.59	87.25	12.75	88.83	11.17	88.30	11.70
	86.95	13.05	87.73	12.27	88.36	11.64	89.07	10.93
	86.75	13.25	87.52	12.48	88.14	11.86	88.65	11.35
	86.83	13.17	87.48	12.52	88.20	11.80		
	86.86	13.14	87.61	12.39	87.84	12.16		
	86.36	13.64	87.41	12.59	87.67	12.33		
	86.71	13.29	87.55	12.45	87.75	12.25		
	86.75	13.25	87.00	13.00				
No. of analyses	12		12		11		7	
Mean	86.64	13.36	87.49	12.51	88.11	11.89	88.67	11.33
Standard Deviation	.22		.23		.32		.27	

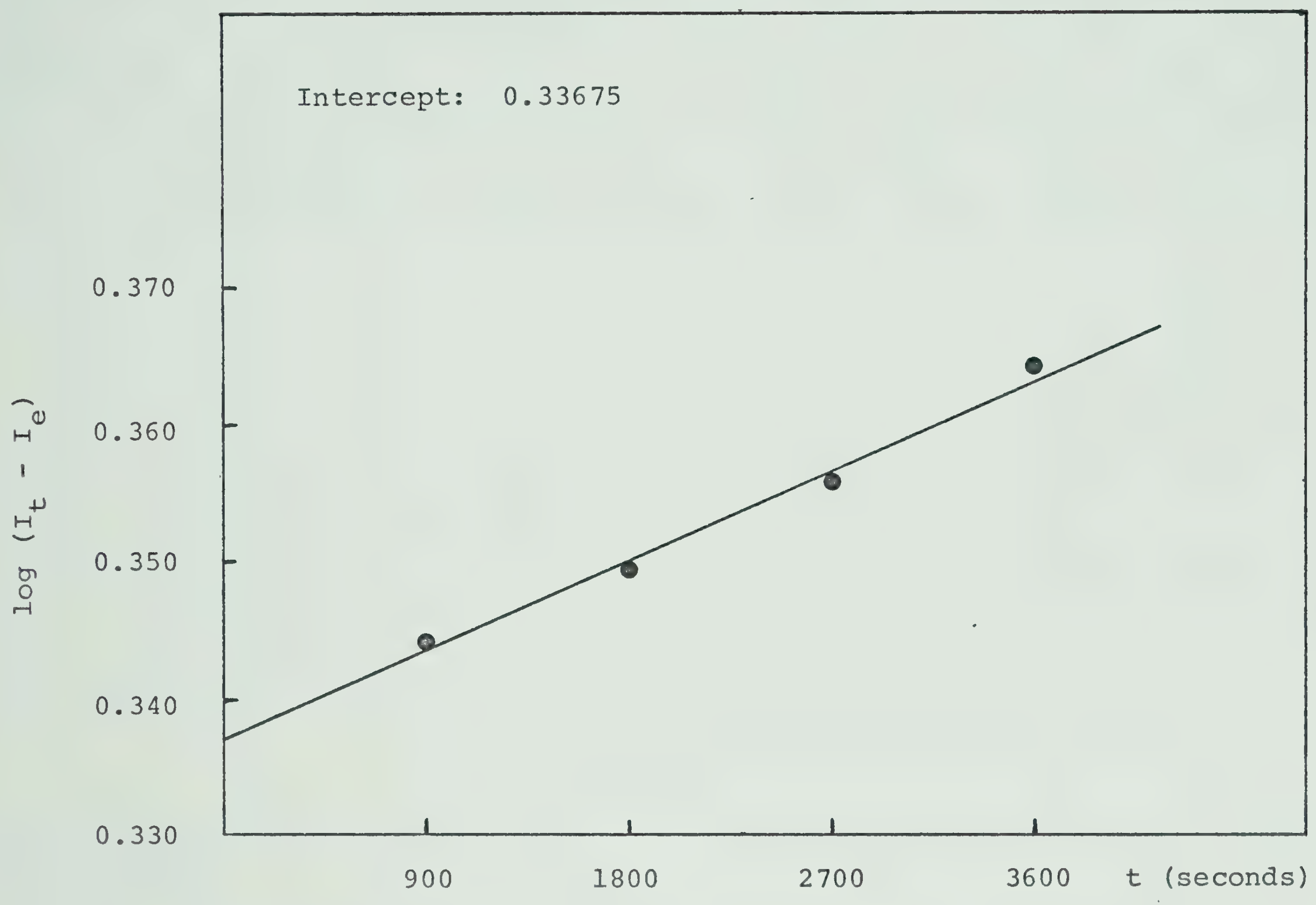

Figure A-3. Plot of Product Distribution versus Thermolysis Time of 41 at 190.10±.02° (see RESULTS, page 24).

Table A-4

Product Distribution of 41 Thermolyzed at 175.06±.02°

Time (sec)	3600		2700		1800		900		600	
Product (%)	46	47	46	47	46	47	46	47	46	47
	88.94	11.06	89.43	10.57	89.49	10.51	89.77	10.23	89.49	10.51
	89.30	10.70	88.94	11.06	89.28	10.72	89.64	10.36	89.91	10.09
	88.94	11.06	88.43	11.57	88.76	11.24	89.43	10.57	89.16	10.84
	89.37	10.63	88.31	11.69	88.92	11.08	89.92	10.08		
	89.12	10.88	88.86	11.14	88.98	11.02	89.80	10.20		
	88.81	11.19	89.11	10.89	88.89	11.11	89.52	10.48		
	89.08	10.92	88.42	11.58	89.15	10.85	89.42	10.58		
	88.71	11.29	88.43	11.57	89.04	10.96	89.58	10.42		
	88.86	11.14	89.11	10.89	88.93	11.07	89.64	10.36		
			89.51	10.49	88.89	11.11	89.41	10.59		
			89.04	10.96	89.53	10.47				
			88.50	11.50						
No. of Analyses	9		12		11		10		3	
Mean	89.01	10.99	88.84	11.16	89.08	10.92	89.61	10.39	89.52	10.48
Standard Deviation	.22		.42		.26		.18		.38	

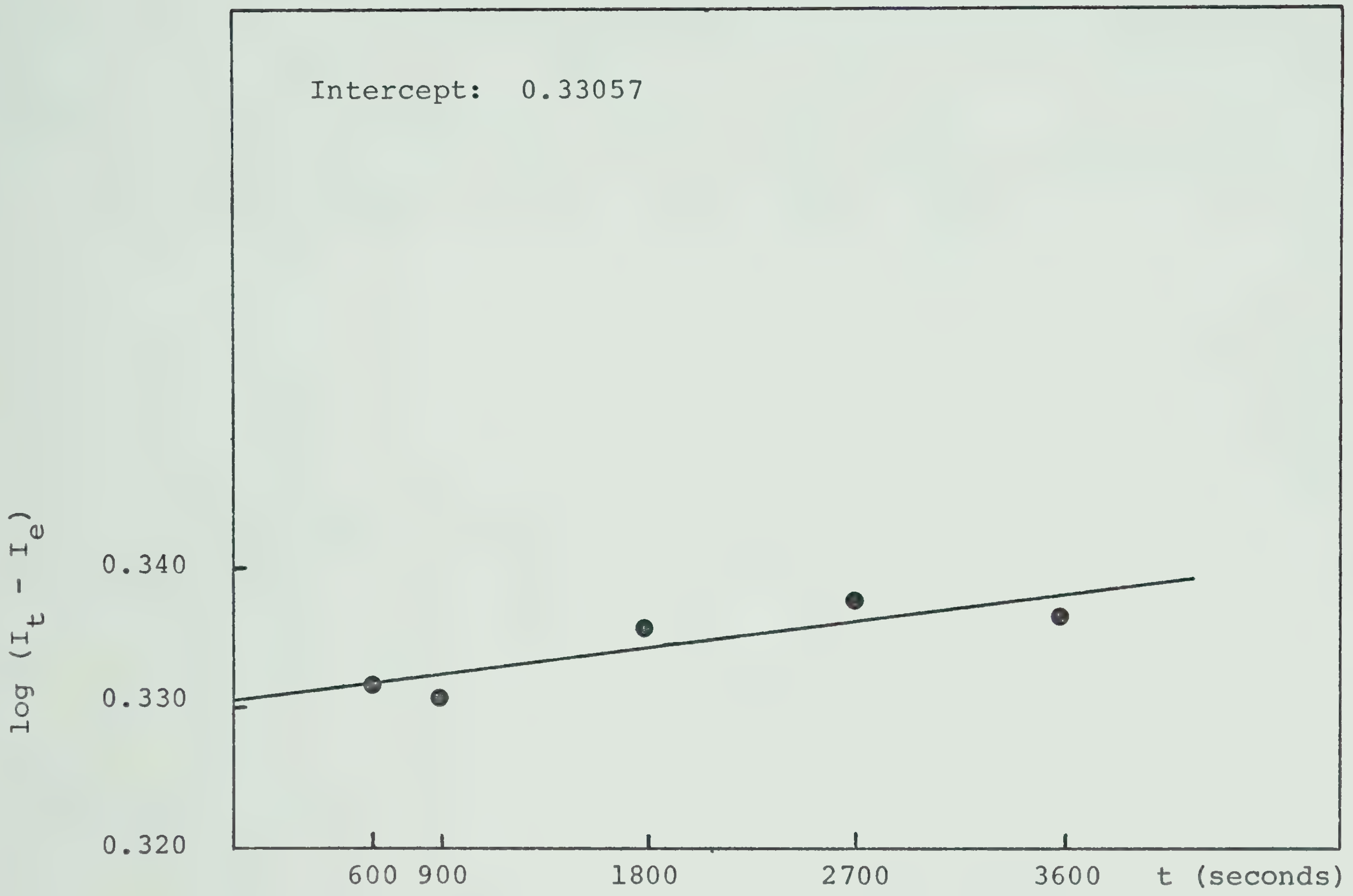

Figure A-4. Plot of Product Distribution versus Thermolysis Time of **41** at 175.06±.02° (see RESULTS, page 24).

Table A-5

Product Distribution of **41** Thermolyzed at 160.10±.02°

Time (sec)	3600		1800		900	
Product (%)	**46**	**47**	**46**	**47**	**46**	**47**
	90.07	9.93	90.09	9.91	90.08	9.92
	90.53	9.47	90.33	9.67	90.08	9.92
	90.15	9.85	89.82	10.18	89.95	10.05
	90.36	9.64	89.79	10.21		
	90.07	9.93	89.67	10.33		
	89.53	10.47	90.41	9.59		
	89.83	10.17	89.18	10.82		
	90.30	9.70	89.89	10.11		
	90.48	9.52	89.88	10.12		
			90.72	9.28		
No. of Analyses	9		10		3	
Mean	90.15	9.85	89.98	10.02	90.04	9.96
Standard Deviation	.32		.43		.08	

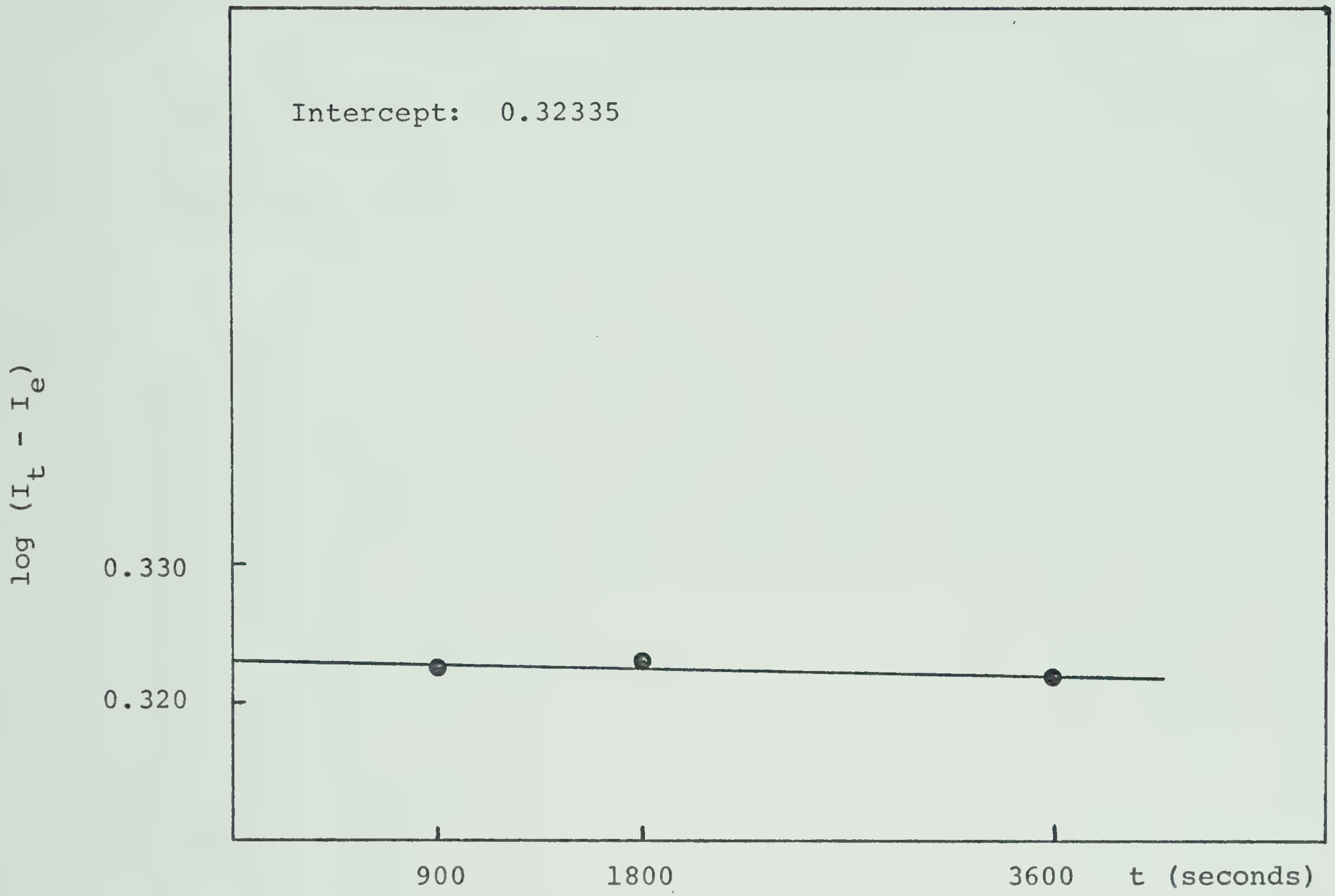

Figure A-5. Plot of Product Distribution versus Thermolysis Time **41** at 160.10±.02° (see RESULTS, page 24).